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PRESSURE-SHIFT OF SPECTRAL LINES

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There have been three different explanations proposed to account for the broadening and displacement toward longer wave-lengths of spectral lines when their radiant atoms are under heavy pressure due to a surrounding gas. The first explanation seems to have been proposed by Fitzgerald¹ and later to have been indorsed by Larmor. This explanation attempts to find the cause of the slower luminous oscillations under heavy pressure in the increase of the specific inductive capacity of the medium in which the oscillations take place.

Fitzgerald says:

When a body is a source of electromagnetic radiations the frequency of its vibrations depends in general on the specific inductive capacity of the medium in which it is immersed. An electromagnetic oscillator performs oscillations that can be calculated from a formula of the form $N^{-2} \propto LC$, where L is self-induction and C is capacity. If the medium have a high electric inductive capacity C will be large and consequently N will be small. Now an increase in the pressure of a gas increases its specific inductive capacity and must in consequence alter to some extent the period of vibration of the molecules in it, if their period of vibration depends at all on electric forces due to constant charges. We can consequently conclude that here is a *vera causa* for some shift towards the red in molecules causing light, for in them there can be no doubt that electric forces are at least a part of the forces affecting the periods of vibration.

¹ *Astrophysical Journal*, 5, 210, 1897.

Larmor¹ later undertakes to show that "the dielectric influence of the neighboring molecules is a *vera causa* of the right order of magnitude" to account for the pressure-shift. He says, speaking of the change in the period of oscillation of whatever produces the spectral lines:

The change must be connected with electric properties of the surrounding gas; mechanical pressure arises merely from the translatory motions of the molecules, and these are so slow as hardly to count in connection with radiation-periods. Thus the phenomenon is probably more strictly describable as a density effect. Electrically, the effect of increase of density is to increase the inductive capacity of the medium, that is, to diminish the effective ethereal elasticity which propagates the radiation. This is the averaged result; each molecule individually, through the agency of its plastic field of force or ether-strain, provides a yielding region in the ether in which the effective stiffness is diminished. The elastic energy which maintains the free vibrations of a radiator is located in its field of force in the adjacent ether; and by dynamical principles any loosening of the constraint in that field such as an adjacent molecule would produce, which would itself be somewhat intensified by equality of period, must in general tend toward increasing the free period, involving the displacement of the radiation toward longer wave-length.

I have quoted at length from Fitzgerald and Larmor because the theory proposed by them is the one I wish especially to discuss. There have been, however, two other theories proposed which deserve notice in any discussion of this question. Humphreys² concludes that "the pressure-shift shows that specific inductive capacity has but little, if any, influence on the period of whatever it is to which these lines are due," and undertakes to explain the displacement by the magnetic action of the molecules on each other. He adopts the theory that the luminous atom is of the so-called "Saturnian" type, consisting of a large number of electrons revolving in circular or broadly elliptical orbits in a common plane about a central positive subatom, and then argues that these magnetic atoms must act upon each other in the Zeeman manner, producing a separation of individual lines as in a strong magnetic field. In a later paper³ he calculates the effect which these molecular fields must have upon each other, and concludes that if the

¹ *Astrophysical Journal*, 26, 120, 1907.

² *Ibid.*, 26, 18, 1907.

³ *Ibid.*, 27, 194, 1908.

average magnetic field of a molecule in the region surrounded by its ring of rotating electrons is as great as 45×10^7 , the pressure-shift may be accounted for after the manner of the Zeeman separation.

Aside from the improbability that the atoms of all metals are ten thousand times as strongly magnetic as the strongest electromagnet ordinarily used in the laboratory for producing the Zeeman effect, is the further difficulty that King¹ has compared the Zeeman separation of a large number of lines with the pressure-shift of the same lines at 42 atmospheres as given by Humphreys and finds the ratio of the Zeeman displacement to the pressure-shift as not even approximately constant even for lines in the same element. Thus for iron the values of this ratio run from 0.78 to 15.5, while several lines were observed which show pressure-displacements, two of them large, but which show no Zeeman separation even in a field of 20,000 gauss.

A third explanation has been proposed by Richardson,² which bases the pressure-shift on the reaction upon the emitting atom of forced vibrations which it has set up by electrostatic induction in neighboring atoms. Richardson's calculations, based upon assumptions regarding the atomic structure and atomic distances which seem to him reasonable, give magnitudes for the pressure-shift from 5 to 200 times as great as the observed values, and require that the displacement shall increase as the third power of the wavelength instead of approximately as the first power, as shown by experiment.

All three of the above-mentioned theories make the change in the period of the vibrating mechanism depend upon the proximity of atoms of its own kind, since the greater the atmospheric pressure around the arc the denser must be the metallic vapor in the interior of the arc. It would accordingly seem to follow from Humphreys' theory that the greatest shift should occur in those metals whose atoms are most strongly magnetic, while from Fitzgerald's theory the greatest shift should occur in those metals whose vapors have the highest specific inductive capacity. Since at the same pressure

¹ *Ibid.*, 31, 433, 1910; also 33, 250, 1911.

² *Phil. Mag.*, 14, 557, 1907.

there should be very approximately the same number of molecules in unit volume of the different vapors, it should be possible to decide between these theories if we knew the magnetic and inductive properties of the different metals. The magnetic properties are already known, and a glance at Humphreys' data in *Astrophysical Journal*, 6, 220 or 224, will show that the pressure-shift is not greater for the magnetic metals than for the others. On the contrary, it is distinctly less. Thus from the data on p. 224 the average shift for *Fe*, *Ni*, and *Co* is 0.026 Å, while for all the lines of all the metals given the average shift is 0.045 Å. Even on the assumption that the magnetic field of the average atom of non-magnetic or diamagnetic material is ten thousand times as great as that of the most magnetic metals when saturated, we might still expect the atoms of the magnetic metals to have stronger fields than the average of all the metals, instead of only half as strong.

The specific inductive capacity of the metals has not been measured, and can only be inferred from their other properties, but any assumption as to the nature of specific inductive capacity must enable one to draw conclusions as to its effect upon other properties of the metal. Thus if we adopt Maxwell's theory, which has been so clearly stated in the quotation from Larmor, that an increase in specific inductive capacity is due to a weakening of the electric elasticity of the ether around the atoms of bodies, we can deduce its effects upon other properties of the body. It seems as clearly established as anything in electrical theory that the forces of affinity and cohesion are attractions between the electropositive and electronegative parts of atoms and molecules. If, for example, the positive subatoms of a metal are held together by their mutual attractions for the same electrons (which seems to be the only conceivable explanation for cohesion in the light of our present knowledge) and if the positive charges of the atoms are of the same order of magnitude, cohesion must be weakest in those metals whose specific inductive capacity is greatest. Such metals should accordingly have greater compressibility, lower melting points, greater expansion coefficients, and should be softer than other metals in which the specific inductive capacity is less. The metals having higher specific inductive capacity should also hold their electrons

with weaker forces than those in which the specific inductive capacity is less, and should accordingly become more electropositive under the action of ultra-violet light. They should also lose electrons when their surfaces are put in contact with metals of lower specific inductive capacity and become the electropositive metals in the voltaic series. For the same reason, when placed in liquids of high specific inductive capacity, thus having their surface cohesion weakened further, they should most easily part with their electropositive subatoms and become the electronegative metals in the electrolytic series. The voltaic series should accordingly correspond with the inductive series.

This fact has been observed for the non-metallic elements. Thus in 1898 Coehn¹ announced the law that for non-metallic elements those having a higher dielectric constant become positively charged when brought into contact with substances having a lower dielectric constant.

In a paper prepared for the meeting of the American Physical Society² in February 1908, the present writer exhibited a table

Element	Compressibility $\times 10^6$	Melting Point	Expansion Coefficient	Hardness	Pressure-Shift
Caesium.....	61	26.5	0.2	161
Rubidium.....	40	38.5	0.3	132
Potassium.....	31.5	58	0.5	132
Sodium.....	15.5	95	0.000072	0.4	108
Lithium.....	8.8	180	0.6	85
Zinc.....	1.5	419	0.000029	2.5	57
Lead.....	2.2	330	0.000028	1.5	60
Tin.....	1.67	230	0.000022	1.8	55
Iron.....	0.38	1500	0.000012	4.5	25
Silver.....	0.82	950	0.000019	2.5-3	39
Copper.....	0.54	1054	0.000017	2.5-3	33
Gold.....	0.47	1035	0.000015	2.5-3	40
Platinum.....	0.21	1780	0.000009	4.3	20

including all the metals whose positions in the voltaic series are well known in which the relation of the voltaic series to the cohesion series is shown. This table is reproduced above as then given and a final column is added showing the displacement of the lines of

¹ *Wied. Ann.*, **64**, 231, 1898.

² *Physical Review*, **26**, 410, 1908.

these same metals for a pressure of 12 atmospheres and a wavelength of 4000 Å as given by Humphreys in *Astrophysical Journal*, 6, 220, 1897.

As will be seen, the agreement of the pressure-shift with the other properties is very close. Iron is the one conspicuous example of misplacement in the voltaic series, the relative positions of zinc, lead, and tin being uncertain. Iron, as is well known, may exist in an active or a passive condition as concerns its avidity for chemical combination with acids. In its passive state it acts very much like gold or platinum and would be placed with these metals in the voltaic series, but its active condition has generally been regarded as the normal one and the passive state as an induced condition. Recently Grave¹ has shown that the passive state is probably the normal condition of iron, and that the active, or electropositive, state is induced, probably by the absorption of hydrogen. If this is correct, iron will take the place in the voltaic series between gold and platinum to which its other properties seem to entitle it.

It will be seen from Humphreys' data on pressure-shift that this is, like many of the other properties of the atoms, a periodic property, the elements of the same periodic group showing a similar pressure-displacement for their spectral lines. In most cases the elements of a well-marked group do not differ widely in their contact electromotive force, and consequently in their specific inductive capacity. The group of alkali metals and the electronegative halogen group at the other extremity of the electrochemical series are exceptions. Since we have no data on the pressure-shift of the latter group, it may be worth while to compare the pressure-shift of the lines of the alkali metals with other properties of these elements.

The variation of the pressure-displacement with the compressibility, the melting point, and the hardness of these metals has already been shown. Fitzgerald, in the paper already cited, says: "In some of the cases I have tried there seems to be some connection between the refractive index of the gas and the amount of the shift." It is plain that if the shift is due to an increase of specific inductive capacity the refractive index of the gas should vary in

¹ *Zeitschrift für physikalische Chemie*, 77, 513, 1911.

the same direction as the pressure-shift. But little is known of the refractive index of metallic vapors; but Gladstone, Edwards, Eisenlohr, and others have calculated the atomic refraction constants for a number of elements from the refractive indices of their compounds, and while different investigators sometimes reach different values in the case of individual elements, their data all show a general agreement. Only Gladstone's data give the refraction equivalents of all the alkali metals. The column marked "Refraction Constant" in the table which follows is taken from his values of the refraction equivalents of the elements given in the *Philosophical Transactions* of 1870.

There is much other evidence to show that the compounds of the electropositive elements have higher refraction equivalents than the corresponding compounds of the electronegative or less electropositive elements. Thus in a table of the refraction equivalents of salt solutions in water given in Ostwald's *Solutions*, p. 272, the refraction equivalents of twelve pairs of corresponding salts of potassium and sodium are given, and in every case the potassium salts give a higher refraction than the corresponding sodium salts by a quantity which is almost constant, the ratio being on the average 33.11:27.78.

Another source of information as to the inductive capacity of an atom may be found in its atomic volume. T. W. Richards¹ has from time to time called attention to evidence which seems to indicate that the atomic volume of an element may be varied by the cohesion pressure upon it when in a compound. Whether this is true or not, if the atoms are built up of positive and negative subatoms held together by electrical forces (as is certainly the case with the atoms of radioactive elements) the volume of an atom should be greater as its specific inductive capacity is greater. Accordingly, in elements of the same group the atomic volume should give an indication of the inductive capacity of the atom. The relation of the atomic volume to the pressure-shift is also shown in the table which follows.

Still another evidence is available for comparing the pressure-shift with the electric properties of the atoms. In two recent

¹ See his Faraday lecture printed in *Science*, 34, 537, October 27, 1911.

papers¹ I have undertaken to show that the positive subatoms of the elements which enter into the electrolytic process as positive ions have specific charges which may be approximately calculated, and that these charges vary with cohesion and hence with specific inductive capacity; in other words, that the specific inductive capacity of the ether is greater about an atom the greater its positive charge. This is further shown in the fact that in the negative halogen group the compressibility decreases and the melting point and cohesion (as shown by the state of aggregation) increase with the atomic weight. Column 6 of the table below gives values, which are only relative, of these charges as calculated from the velocity of the ions in a water solution under a given electromotive force.

In the papers last mentioned and elsewhere² attention has been called to the fact that all these properties are functions of the square root of the atomic weight. Thus the melting points of the alkali metals may be calculated to within the differences of determination of different investigators by the equation $T_a = \frac{531 \cdot 5}{\sqrt{w}} + 252 \cdot 5$, where T_a is the absolute temperature of the melting point and w is the atomic weight of the metal.

I have accordingly given the square root of the atomic weight of the metals in the second column of the following table, and for the sake of completeness I have again given the melting point, compressibilities, and hardness which were given in the preceding table for the voltaic series.

	\sqrt{w}	Pressure-Shift	Refraction Constant	Atomic Volume	Atomic Charge	Compressibility $\times 10^6$	Hardness	Melting Point
Cs.....	11.5	161	13.8	70.6	157	61	0.2	26.5
Rb.....	9.24	132	14.1	56	101	40	.3	38.5
K.....	6.24	132	8.2	45.4	44	31.5	.5	58
Na.....	4.8	108	4.8	23.7	18	15.5	.4	95
Li.....	2.6	85	3.8	12.9	5	8.8	.6	180

Taken all together, there accordingly seems to be a considerable amount of evidence to show that the pressure-shift of the spectral

¹ *Physical Review*, **32**, 512, 518, 1911.

² "A Physical Theory of Electrification," published by the Leland Stanford Jr. University, University Series, No. 6, 1911.

lines is related to just those properties of the atoms which seem to depend upon the specific inductive capacity.

An objection which will at once suggest itself to everyone is the fact that the lines are, though to a less extent, broadened toward the violet. An increase of specific inductive capacity should slow down the oscillations but should not accelerate them, while Humphreys' magnetic theory would displace the lines in both directions. It is well known, however, that the specific inductive capacity of the air and of ordinary gases is very small as compared with that of metallic vapors. Accordingly, when an air molecule enters the field of force of a radiating metallic atom the specific inductive capacity of its field of force should be decreased, and this should accelerate the vibration period of the atom. If this point of view is correct, it would seem that the greatest shift toward the red should be due to those atoms in the center of the arc, while the greatest shift toward the violet should be due to atoms around the outer surface. Perhaps this difference may be capable of observation.

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AN INVESTIGATION OF THE SPECTRA OF IRON AND TITANIUM UNDER MODERATE PRESSURES¹

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The results which are contained in this article are the main products of a study of the effect of a gaseous pressure of 9 atmospheres upon the arc spectrum of iron and of pressures of from 3 to 17 atmospheres upon the arc and spark spectra of titanium. The investigation was begun in the spring of 1910 and carried on during a period of three months of that year and a corresponding period of 1911. At first the end in view was to study the effects of pressure upon the spark spectrum alone, but the lack of corresponding results for the arc at moderate pressures required the extension of the investigation to include arc results as well.

Previous studies of the pressure effect have for the most part been at comparatively high pressures. Thus the recent results of Rossi² upon the arc spectra of titanium and vanadium are based principally upon pressures between 25 and 100 atmospheres. A part of the earlier work of Humphreys,³ and Humphreys and Mohler,⁴ dealt with pressures as low as 4 atmospheres, but all of the more recent work of Humphreys⁵ has been at much higher pressures. Similarly the work of Duffield⁶ upon the arc spectra of iron, gold, and silver contains some results obtained at 5, 10, and 15 atmospheres, but the great majority of his values are also for high pressures. In the case of the spark spectrum only two previous investigations are available. The first of these, by Hale and Kent,⁷ deals with a small number of iron lines at pressures of from 3 to 53 atmospheres; the second, by W. B. Anderson,⁸ gives the displacements of a considerable number of iron lines at 50 atmospheres.

¹ *Contributions from the Mount Wilson Solar Observatory*, No. 58.

² *Proc. Roy. Soc.*, A **83**, 414, 1910.

³ *Astrophysical Journal*, **4**, 249, 1896; **6**, 169, 1897.

⁴ *Ibid.*, **3**, 114, 1895.

⁵ *Ibid.*, **22**, 217, 1905; **26**, 18, 1907.

⁶ *Ibid.*, **26**, 375, 1907; *Phil. Trans.*, A **208**, 111, 1908.

⁷ *Astrophysical Journal*, **17**, 154, 1903.

⁸ *Ibid.*, **24**, 221, 1906.

With the exception of some results by Humphreys¹ for certain lines of iron and chromium in the green and yellow parts of the spectrum all of the values given in these researches are for the more refrangible lines.

In view of these considerations it has seemed desirable to us to carry on our work at relatively low pressures and to include as large an extent of spectrum as possible. A combination of our own results with those obtained at higher pressures by other observers would give a severe test of the law of the proportionality of displacement to pressure, while the values of the displacements for lines of widely different wave-lengths would provide more satisfactory material for a discussion of the variation of displacement with wave-length than could a comparatively limited range of spectrum.

The astronomical applications of pressure results also make these considerations important. So far as our knowledge extends, the effective pressures in the reversing layer of the sun and in stellar atmospheres are moderate in amount. For example, the most recent determination of the pressure in the reversing layer of the sun by Fabry and Buisson² gives a value of 5 atmospheres. Accordingly pressures of the same order should be employed in the laboratory work in case a direct comparison of the character and the displacements of the lines is to be made with those in solar and stellar spectra.

The investigation has been carried on in the Pasadena laboratory of the Mount Wilson Solar Observatory and the spectrograph employed is the 9.1 m plane grating Littrow instrument already used by Mr. King and Mr. Babcock in numerous studies of the Zeeman effect. Since this spectrograph has been described in a previous publication,³ no details are necessary in this place. The grating is a 20 cm plane grating by Michelson with 500 lines to the millimeter, and the second order has been used for all of the photographs taken in connection with this work. The linear scale given by the spectrograph is approximately 1 mm = 0.95 Ångström.

¹ *Ibid.*, 26, 18, 1907.

² *Ibid.*, 31, 97, 1910.

³ *Contributions from the Mount Wilson Solar Observatory*, No. 23; *Astrophysical Journal*, 27, 204, 1908.

The pressure-chamber consists of a strong brass hood with a flange at its base which is fastened by a series of iron clamps around its rim to a brass base carrying a similar flange. The two portions have been surfaced accurately and at the junction a thin lead washer provides an air-tight union. The top of the hood carries the pressure gauge and the connections for attaching the tanks of compressed gas. The connections for the electrodes are passed through the sides of the box and are very heavily insulated in order to provide for the use of high potential for the spark. The electrodes themselves consist of copper clips placed in a horizontal position, and the arc or spark passes directly between small pieces of metal held in these clips. The distance between the electrodes may be varied by means of a fiber handle on the outside of the box which turns a screw acting through a hard rubber sleeve. At moderate pressures the chamber shows very little leakage.

In the front of the brass hood is the window through which the light from the arc or spark passes to the spectrograph. Since the spectrograph itself contains a glass lens and so is not adapted for work in the extreme ultra-violet part of the spectrum, the window also is made of glass. It is about 2 cm thick and conical in shape, with its base toward the light-source in order to withstand the effect of the pressure from within. The window is mounted in the center of a round brass casting about 12 cm in diameter cut with a quarter thread. This engages with a similar thread in an opening in the pressure-chamber and the block is tightened by means of a powerful wrench, until an air-tight junction is obtained. By taking off this block it is possible to reach the electrodes without unclamping the entire box.

The light passing through the window of the pressure-chamber is focused upon the slit of the spectrograph by means of a glass lens placed midway between window and slit. It has been found possible in all of the work to obtain arc and spark gaps sufficiently wide to avoid the necessity for magnification at the slit of the spectrograph. The diameter of the lens is such that the cross-section of the cone of light at the base of the spectrograph is about six times that of the grating surface, and we have given especial care to the adjustment of the instrument in order to keep the

illuminated area as nearly as possible concentric with the grating throughout all of the observations. To provide for accurate guiding during an exposure when the arc or spark shifts from one point to another upon the electrodes, we have adopted the simple expedient of placing the condensing lens upon a double-slide rack. The observer watches the image upon the slit with a small telescope and corrects for the motion of the arc or spark by a slight vertical or horizontal motion of the lens. It is evident that the effect of such motion is to displace the cone of light slightly with respect to the grating, but the margin of full illumination is so great and the motion of the lens so small that no error is to be feared from this source.

The arc used throughout this investigation was produced by a direct current of 110 volts furnished by a motor generator. A bank of lamps placed in series in the circuit provided the means of varying the amount of current passing through the arc. In general a current of from 4 to 8 amperes has been used for most of the work. By increasing or decreasing the current it is usually possible to vary the amount of reversals of the stronger comparison lines, and this has proved most useful in a part of the investigation.

The alternating current for the spark was furnished by a 5 kilowatt transformer fed by an alternating current of 220 volts. It is capable of giving a potential as great as 64,000 volts. For most of this work either 16,000 or 32,000 volts have been employed. A self-induction coil placed in the secondary circuit has been used for a part of the work for the purpose of reducing the intensities of the enhanced lines. It may be well to state at this point that we have been able to find no distinct evidence of the variation of pressure displacements with change of current, capacity, potential, or arc or spark-gaps for the range throughout which we have worked. Nor does there appear to be any difference between the results for an atmosphere of air or of carbon dioxide. The effect of a hydrogen atmosphere is discussed at a later point.

A considerable number of photographs of an arc between carbon poles was taken, and the displacements of the lines of iron, which occurred as an impurity, were found to be the same as those obtained from an arc with iron poles. Table I contains the results from arcs with iron and with carbon poles.

On all of the photographs the spectrum under pressure is placed in the center with the comparison spectrum of arc or spark at atmospheric pressure on either side, a simple occulting-bar arrangement providing for covering and uncovering the different portions of the slit. The exposure for the comparison spectrum has been divided into two parts, one-half before and one-half after the exposure for the pressure spectrum. In order to test the possible effect upon the photographs of accidental disturbances such as the vibration of the building, we have made a number of exposures upon an arc spectrum separated by considerable intervals of time, but measures of the photographs have shown no appreciable displacements since the spectrograph was definitely adjusted for this work. In general the exposure times, both for the comparison and the pressure spectrum, have been comparatively short. For the arc spectrum in the blue and violet regions they have varied from 1 to 2 minutes for the pressure spectrum to 1 to 6 minutes for the comparison spectrum on Seed "Process" plates. For the less refrangible regions the exposure times are, of course, longer, reaching in the case of the comparison spectrum a maximum of some 40 minutes in the red. The spark spectrum requires considerably more time, and in the red we have been obliged to give as much as $1\frac{1}{2}$ hours to the comparison spectrum of iron.

The great amount of labor involved in the measurement and reduction of the photographs has made it impossible to determine the values of the displacements of all of the lines at all of the pressures employed. Accordingly we have adopted the plan of making as complete a study as possible of all well-measurable lines at a single pressure, and for the other pressures using a selected list sufficient in number to give a mean of high precision for purposes of comparison. The pressure adopted for the principal series was 8 atmospheres above atmospheric pressure, a value sufficiently high to give displacements of considerable amount, but not too high to prevent direct comparison with the results for solar lines. The other pressures used have been 2, 4, 6, 12, and 16 atmospheres above atmospheric pressure and a few photographs have been taken at a partial vacuum. As already stated, no appreciable difference could be detected between the displacements for an atmosphere of air or

carbonic dioxide, and the latter gas has been used throughout the greater part of the investigation.

The extraordinary variety in behavior of different spectrum lines under pressure has, of course, been noted by all observers. In general the lines may be divided roughly into five broad classes:

1. Lines which are symmetrically reversed.
2. Lines which are unsymmetrically reversed.
3. Lines which remain bright and fairly narrow under pressure.
4. Lines which remain bright and symmetrical but become wide and diffuse under pressure.
5. Lines which remain bright and are widened very unsymmetrically toward the red.

The lines in the first class are those which are most readily measurable and for which the degree of precision is highest. They are much more numerous in the arc spectrum of titanium than in that of iron, and in general they are likely to be among the strongest of the lines in the spectrum. The number of lines in the second class is smaller than that in the first and the reversals as a rule are fainter. Most of the enhanced lines in the spark spectrum of titanium belong to this class.

The lines in the third and fourth classes form a majority of all of the lines measured, particularly in the less refrangible part of the spectrum where reversals are comparatively few. The lines in the third class usually are well measurable, those in the fourth less so. The distinction between these two classes is entirely arbitrary as all lines are widened somewhat under pressure.

The fifth class is of great interest. Almost all of the lines belonging to it occur in the yellow and red portions of the spectrum, and all show enormous displacements. The widening of these lines and their lack of symmetry are so great, however, that many of them are practically incapable of measurement, and for the others the degree of accuracy is extremely low. The measures when made are upon the maximum, which is always upon the violet side of the center of the line.

Most of the characteristics of the lines in the arc under pressure apply equally well to the same lines in the spark. All lines in the spark spectrum are much more diffuse, however, and the degree of

accuracy of measurement is distinctly lower. This is especially true of the enhanced lines of titanium, which as a rule show very faint unsymmetrical reversals, which it is extremely difficult to measure with precision.

In the tables which follow are given the results of our measures of the displacements of the principal lines in the spectra of the iron arc and the titanium arc and spark for a total pressure of 9 atmospheres, the comparison spectrum being in each case the same source at atmospheric pressure.

The wave-length of the line according to Rowland's table is given in the first column; its type as regards reversal and symmetry, referred to one of the five classes above, in the second column; its mean displacement in the fourth column; the mean deviation of the separate determinations from the mean in the fifth column, the unit being 0.001 Ångström; and the number of plates in the sixth column. In the discussion of these displacements with relation to their variation with wave-length the lines are treated in different groups. In order to save repetition at a later point the group under which each line is treated is given in the third column. The seventh, eighth, and ninth columns in the table for titanium give the displacements of the corresponding lines in the spark spectrum, the average deviations of the separate determinations from the mean, and the number of plates measured. A few lines not given by Rowland are taken from the lists of Hasselberg¹ and Evans.²

In general each plate was measured four times, once in each direction, by two different observers.

Although we shall not attempt in this place to enter into any extended discussion of the characteristics of the various lines under pressure, there are a few general results evident from an inspection of these tables to which reference may be made.

1. Reversal is clearly a function of wave-length for both arc and spark. The number of reversed lines falls off rapidly toward longer wave-lengths, there being extremely few reversals in the red portion of the spectrum, for either iron or titanium. The general law was

¹ *Astrophysical Journal* 4, 212, 1896.

² *Ibid.*, 29, 160, 1909.

TABLE I

IRON

λ	Class	Group	Δ	Mean De- viation ±	No. of Plates	λ	Class	Group	Δ	Mean De- viation ±	No. of Plates
3609.008	I	b	0.008	1	3	4202.198	I	b	0.025	9	6
3618.919	I	b	0.011	1	3	4204.101	3	b	0.017	1	2
3631.605	I	b	0.015	1	3	4210.494	5	c	0.053	2	2
3647.988	I	b	0.012	4	3	4216.351	3	b	0.015	2	2
3680.069	I	a	0.007	2	3	4227.606	5	d	0.11	10	6
3687.610	I	b	0.016	1	3	4233.772	5	d	0.09	20	7
3705.708	I	a	0.007	2	3	4236.112	5	d	0.09	20	8
3709.389	I	b	0.013	1	3	4250.287	5	c	0.070	4	2
3720.084	I	a	0.014	1	3	4250.945	2	b	0.022	4	10
3722.720	I	a	0.010	2	3	4260.640	2	c	0.051	8	8
3727.778	I	b	0.014	2	3	4271.934	1	b	0.022	3	10
3733.469	I	a	0.007	1	3	4282.565	1	b	0.021	4	7
3735.014	I	b	0.013	2	3	4291.630	3	a	0.014	0	1
3737.281	I	a	0.016	2	3	4294.301	2	b	0.029	5	6
3743.508	I	b	0.015	1	3	4299.410	5	d	0.09	20	6
3745.717	I	a	0.008	1	3	4308.081	1	b	0.021	5	7
3746.058	I	a	0.008	1	3	4315.262	3	b	0.019	3	7
3748.408	I	a	0.010	1	3	4325.939	1	b	0.020	4	7
3749.631	I	b	0.017	2	3	4337.216	3	b	0.027	2	7
3758.375	I	b	0.022	2	3	4352.908	3	b	0.017	3	7
3763.945	I	b	0.017	1	3	4369.941	3	b	0.023	3	5
3765.689	I	b	0.013	2	3	4376.107	3	a	0.018	2	7
3767.341	I	b	0.017	1	3	4383.720	1	b	0.027	4	7
3788.046	I	b	0.016	1	3	4404.927	1	b	0.021	3	7
3795.147	I	b	0.015	2	3	4407.871	4	c	0.053	2	2
3815.987	I	b	0.024	2	3	4408.582	4	c	0.058	2	2
3826.027	I	b	0.021	4	4	4415.293	1	b	0.018	5	7
3827.980	I	b	0.019	2	4	4422.741	3	b	0.018	3	2
3834.364	I	b	0.016	5	4	4427.482	3	a	0.017	3	7
3886.434	I	a	0.011	3	10	4430.785	4	c	0.048	8	4
3887.196	I	b	0.022	4	5	4442.510	4	c	0.053	9	7
3888.671	I	b	0.020	3	6	4443.365	3	b	0.019	4	6
3895.803	I	a	0.011	4	7	4447.892	4	c	0.051	9	7
3899.850	I	a	0.012	5	10	4454.552	3	b	0.023	2	2
3903.090	I	b	0.022	2	6	4459.301	4	c	0.051	8	7
3906.628	I	a	0.011	4	7	4461.818	3	a	0.015	3	7
3920.410	I	a	0.010	3	8	4466.727	4	b	0.018	4	7
3923.054	I	a	0.011	3	9	4476.185	4	b	0.021	3	7
3928.075	I	a	0.012	4	9	4489.911	3	a	0.015	2	2
3930.450	I	a	0.013	3	8	4494.738	4	c	0.053	8	6
3956.819	4	b	0.014	5	5	4528.798	4	c	0.061	4	5
3969.413	I	b	0.022	3	8	4531.327	3	b	0.029	2	4
3977.891	4	b	0.017	4	3	4559.928	5	c	0.100	4	2
3997.547	4	b	0.015	3	4	4871.512	5	c	0.080	5	4
4005.408	I	b	0.019	3	9	4872.332	5	c	0.094	5	4
4045.975	I	b	0.023	4	5	4878.407	5	c	0.087	2	2
4063.759	I	b	0.020	5	5	4890.948	5	c	0.070	8	4
4071.908	I	b	0.021	4	5	4891.683	5	c	0.052	1	4
4132.235	I	b	0.024	5	5	4919.174	5	c	0.072	3	4
4134.840	4	b	0.027	2	2	4920.685	5	c	0.082	5	4
4144.038	I	b	0.029	6	6	4957.480	5	c	0.083	5	4

TABLE I—Continued

λ	Class	Group	Δ	Mean De- viation *	No. of Plates	λ	Class	Group	Δ	Mean De- viation *	No. of Plates
4957.785	5	c	0.086	3	3	5659.052	5	d	0.15	10	2
5227.362	4	a	0.031	5	6	5975.575	4	b	0.054	7	2
5233.122	5	d	0.11	20	4	6027.274	4	b	0.062	6	3
5266.738	5	d	0.13	30	2	6065.709	4	b	0.077	5	4
5269.723	1	a	0.027	3	6	6136.829	4	b	0.082	7	4
5270.558	4	a	0.029	3	5	6137.915	4	b	0.078	3	4
5324.373	5	d	0.12	20	5	6157.945	4	b	0.041	8	3
5328.236	1	a	0.029	3	6	6173.553	4	b	0.067	5	2
5328.696	4	a	0.026	3	3	6191.779	4	b	0.086	4	4
5333.089	4	a	0.029	3	2	6200.527	4	b	0.079	10	2
5340.121	5	d	0.14	20	3	6213.444	4	b	0.072	4	3
5341.213	4	a	0.028	1	3	6219.494	4	b	0.073	2	3
5371.734	1	a	0.029	2	6	6230.943	4	b	0.070	5	4
5393.375	5	d	0.14	10	3	6246.535	5	d	0.28	10	3
5397.344	4	a	0.029	2	6	6252.773	4	b	0.077	3	6
5405.989	4	a	0.027	3	6	6254.456	4	b	0.064	4	5
5429.911	4	a	0.029	2	6	6256.572	4	b	0.089	5	4
5434.740	4	a	0.027	2	6	6265.348	4	b	0.070	4	5
5447.130	4	a	0.031	3	6	6298.007	4	b	0.068	2	1
5455.834	4	a	0.029	1	5	6301.718	5	d	0.25	30	2
5476.500	4	a	0.029	2	3	6318.239	4	b	0.080	4	2
5476.778	5	d	0.11	10	2	6335.554	4	b	0.074	3	2
5497.735	3	a	0.030	2	3	6337.048	5	d	0.26	10	2
5501.683	3	a	0.030	3	3	6393.820	4	b	0.072	7	2
5507.000	3	a	0.031	4	3	6400.217	5	d	0.24	10	2
5535.644	4	a	0.034	4	3	6411.865	5	d	0.23	10	2
5569.848	5	d	0.14	10	5	6421.570	4	b	0.068	2	2
5573.975	5	d	0.14	10	5	6431.066	4	b	0.068	4	2
5576.320	5	d	0.16	10	2	6495.213	4	b	0.065	4	2
5586.991	5	d	0.12	2	2	6546.479	4	b	0.073	3	2
5603.186	5	d	0.15	10	2	6593.161	4	b	0.076	6	2
5615.877	5	d	0.13	20	2	6594.121	4	b	0.070	2	2
5624.769	5	d	0.16	10	2	6678.235	4	b	0.086	1	3
5638.488	5	d	0.15	10	2						

stated by Hale in 1902¹ for the spark under pressure, but Duffield's² observations upon the iron arc between $\lambda 4000$ and $\lambda 4500$ did not appear to indicate the same effect for this source. Apparently the discrepancy is due to the comparatively limited region of spectrum investigated by Duffield.

2. The number of unsymmetrical bright lines increases toward longer wave-lengths. This is true particularly of the high-temperature lines of iron, the low-temperature lines (those relatively

¹ *Astrophysical Journal*, **15**, 227, 1902.

² *Phil. Trans.*, **A 208**, 111, 1908.

TABLE II
TITANIUM

λ	CLASS	GROUP	ARC			SPARK			
			Δ	Mean De- viation ±	No. of Plates	Δ	Mean De- viation ±	No. of Plates	
3729.952	I	a	0.009	1	3	
3741.295	I	..	0.011	1	3	
3753.003	I	a	0.014	4	3	
3753.732	I	a	0.006	2	2	
3759.447	I	..	0.011	4	4	Enhanced line
3761.464	I	..	0.008	1	4	Enhanced line
3771.798	I	a	0.007	3	3	
3808.645	3	a	0.014	3	4	0.019	1	3	
3900.681	3	..	0.034	12	5	0.041	5	4	Enhanced line
3901.114	2	a	0.010	4	5	0.019	4	2	
3904.026	I	a	0.019	4	7	0.023	3	4	
3913.609	3	..	0.036	4	6	0.037	3	4	Enhanced line
3914.477	I	a	0.006	2	6	0.017	2	4	
3921.503	I	a	0.005	2	6	0.013	4	4	
3924.673	I	a	0.010	2	6	0.020	4	4	
3926.465	4	..	0.048	5	5	0.042	2	2	
3930.022	I	a	0.008	3	6	0.018	3	4	
3947.018	I	a	0.004	2	6	0.014	4	4	
3948.818	I	a	0.013	2	7	0.021	6	4	
3950.476	I	a	0.010	2	6	0.021	4	4	
3958.355	I	a	0.015	3	7	0.021	1	3	
3962.995	I	a	0.010	4	6	0.021	1	4	
3964.416	I	a	0.010	3	6	0.022	7	4	
3981.017	I	a	0.016	4	8	0.022	3	3	
3982.630	I	a	0.006	2	6	0.020	2	4	
3989.912	I	a	0.016	3	9	0.016	7	3	
3998.790	I	a	0.016	5	9	0.015	3	3	
4009.079	I	a	0.008	2	5	0.019	1	4	
4009.807	2	a	0.009	2	5	0.020	2	4	
4021.893	4	..	0.051	2	3	
4024.726	I	a	0.008	1	4	0.021	1	4	
4028.497	3	..	0.018	2	2	Enhanced line
4060.415	I	a	0.015	2	4	0.025	4	4	
4065.239	I	a	0.011	2	4	0.023	2	4	
4078.631	I	a	0.005	1	4	0.017	2	4	
4082.589	I	a	0.019	4	4	0.025	3	4	
4099.327	4	a	0.028	3	4	0.025	2	2	
4112.869	I	a	0.014	3	4	0.015	1	4	
4151.129	4	a	0.034	7	4	0.031	2	3	
4159.805	4	a	0.035	4	4	0.025	1	2	
4163.818	4	..	0.041	2	4	Enhanced line
4164.27	4	a	0.031	9	4	
4166.45	4	a	0.030	3	3	
4169.46	4	a	0.034	1	3	
4171.213	4	a	0.035	3	4	0.044	0	2	
4172.066	4	..	0.042	2	3	Enhanced line
4174.61	4	a	0.035	7	3	
4183.45	4	a	0.040	1	3	
4186.280	I	a	0.016	3	5	0.030	1	4	

TABLE II—Continued

A	CLASS	GROUP	ARC			SPARK			
			Δ	Mean De- viation *	No. of Plates	Δ	Mean De- viation *	No. of Plates	
4188.84	4	a	0.044	2	4	
4200.946	4	a	0.030	4	3	
4203.620	4	a	0.038	2	4	0.030	1	2	
4224.792	4	..	0.064	2	3	
4227.822	4	..	0.073	1	3	
4238.00	4	a	0.014	1	4	
4263.290	4	a	0.026	2	2	
4265.832	4	a	0.037	1	2	
4272.701	3	a	0.016	2	4	
4276.587	4	a	0.030	3	4	
4278.390	4	a	0.043	3	4	
4281.530	4	a	0.014	3	4	
4282.860	4	a	0.027	2	4	
4285.164	4	a	0.036	3	4	
4286.168	1	a	0.021	2	4	
4287.566	1	a	0.024	2	4	
4288.310	3	a	0.019	1	4	
4289.237	1	a	0.025	3	4	
4290.080	3	a	0.033	1	4	
4290.377	3	..	0.046	2	5	0.048	9	6	Enhanced line
4291.114	1	a	0.022	2	5	0.016	2	6	
4294.204	3	..	0.029	1	5	0.039	6	6	Enhanced line
4295.914	1	a	0.022	2	5	0.015	3	5	
4298.828	1	a	0.025	2	4	0.019	2	6	
4299.410	1	a	0.023	3	4	0.034	4	6	
4299.803	1	a	0.023	2	4	0.024	3	6	
4300.211	3	..	0.029	4	4	0.051	4	6	Enhanced line
4300.732	1	a	0.021	2	4	0.018	3	6	
4301.158	1	a	0.024	1	4	0.025	2	6	
4302.085	3	..	0.033	2	2	Enhanced line
4306.078	1	a	0.024	2	4	0.027	4	6	
4308.64	3	a	0.019	6	3	
4313.034	3	..	0.047	4	3	Enhanced line
4314.479	3	a	0.018	3	3	
4314.964	1	..	0.032	4	3	
4326.520	3	a	0.029	2	4	0.025	3	6	
4338.084	3	..	0.017	3	4	0.040	8	6	Enhanced line
4346.26	3	a	0.006	2	3	
4360.644	3	a	0.042	4	3	
4394.093	4	a	0.015	3	3	
4395.201	3	..	0.025	2	3	Enhanced line
4399.935	3	
4417.450	3	a	0.027	4	4	0.033	3	6	
4421.928	4	..	0.038	8	3	Enhanced line
4422.985	4	a	0.028	4	3	
4426.201	4	a	0.026	5	3	
4427.266	1	a	0.017	3	7	0.026	1	7	
4434.168	4	a	0.035	4	3	
4440.515	4	a	0.029	5	4	0.027	4	6	
4443.976	4	..	0.021	2	4	0.040	4	6	Enhanced line
4449.313	1	a	0.029	4	8	0.033	3	9	

TABLE II—Continued

λ	CLASS	GROUP	ARC			SPARK			
			Δ	Mean De- viation *	No. of Plates	Δ	Mean De- viation *	No. of Plates	
4451.087	I	a	0.020	2	9	0.037	3	3	
4453.486	I	a	0.040	4	10	0.045	3	9	
4453.876	I	a	0.026	5	5	0.042	2	2	
4455.485	I	a	0.041	2	9	0.048	2	3	
4457.600	I	a	0.039	3	10	0.044	4	9	
4465.975	I	a	0.025	2	10	0.033	4	9	
4468.663	4	..	0.046	4	6	0.050	7	8	Enhanced line
4471.408	I	a	0.024	4	10	0.029	4	9	
4475.026	4	..	0.074	4	5	
4479.870	4	a	0.027	2	5	0.025	1	2	
4480.752	3	a	0.027	4	5	0.032	4	2	
4481.438	I	a	0.023	2	10	0.031	3	9	
4488.493	0.054	7	2	Enhanced line
4489.262	I	a	0.029	5	6	0.033	4	8	
4501.445	4	..	0.046	4	6	0.063	6	8	Enhanced line
4512.906	I	a	0.029	2	10	0.039	4	9	
4518.108	I	a	0.029	2	10	0.039	3	9	
4518.866	3	a	0.025	5	5	0.029	1	2	
4522.974	I	a	0.031	3	10	0.040	4	9	
4527.400	I	a	0.029	3	10	0.041	4	9	
4533.419	I	a	0.031	2	10	0.036	3	9	
4534.139	3	..	0.044	5	6	0.063	3	7	Enhanced line
4534.953	I	a	0.034	3	10	0.036	5	9	
4535.741	I	a	0.029	3	9	0.031	3	3	
4536.094	I	a	0.023	2	4	0.036	2	2	
4536.222	I	a	0.031	1	2	
4544.864	I	a	0.031	2	10	0.035	2	9	
4548.938	I	a	0.031	2	10	0.039	6	9	
4549.808	4	..	0.048	2	6	0.062	8	8	Enhanced line
4552.632	I	a	0.029	3	10	0.041	3	9	
4555.662	I	a	0.029	2	8	0.041	3	9	
4562.814	3	a	0.008	1	5	0.026	5	2	
4563.939	4	..	0.034	4	6	0.053	6	7	Enhanced line
4572.156	4	..	0.051	5	6	0.065	4	8	Enhanced line
4590.126	0.052	5	2	Enhanced line
4617.452	I	a	0.029	2	5	0.038	1	2	
4623.279	I	a	0.027	3	5	0.040	4	2	
4620.521	I	a	0.037	4	5	0.042	4	2	
4638.050	4	a	0.043	3	3	
4645.368	I	a	0.039	6	3	0.043	2	2	
4650.193	4	a	0.037	4	3	0.040	4	2	
4656.644	I	a	0.017	2	3	0.027	2	2	
4667.768	I	a	0.020	4	3	0.023	1	2	
4675.294	4	a	0.030	1	3	0.051	2	2	
4682.088	I	a	0.018	2	3	0.018	1	2	
4691.523	I	a	0.038	2	3	
4698.946	2	a	0.037	2	3	0.036	2	2	
4710.368	I	a	0.041	4	3	0.046	7	2	
4722.797	4	a	0.036	4	3	
4723.359	4	a	0.040	2	3	
4742.979	I	a	0.037	4	3	0.040	2	2	

TABLE II—Continued

A	CLASS	GROUP	ARC			SPARK			
			Δ	Mean De- viation ±	No. of Plates	Δ	Mean De- viation ±	No. of Plates	
4758.308	I	a	0.027	7	5	0.030	0	2	Enhanced line
4759.463	I	a	0.031	4	5	0.036	2	2	
4766.48	3	a	0.036	2	3	
4778.441	4	a	0.040	4	3	
4781.91	3	a	0.034	1	3	
4799.984	4	a	0.038	6	3	0.044	4	2	
4805.285	3	..	0.048	2	3	
4805.606	4	a	0.074	4	6	
4820.593	I	a	0.033	6	9	0.041	1	3	
4836.313	4	a	0.051	7	7	
4841.074	I	a	0.007	2	10	0.018	2	3	
4848.605	4	a	0.020	1	3	
4856.203	I	a	0.020	2	6	
4868.451	I	a	0.026	4	4	
4870.323	I	a	0.020	4	5	
4885.264	I	a	0.026	4	7	
4900.095	I	a	0.018	4	4	
4913.803	I	a	0.022	6	4	
4915.414	3	a	0.021	4	4	
4919.99	4	a	0.020	4	4	
4921.963	4	a	0.020	2	4	
4928.511	4	a	0.032	4	4	
4975.530	4	a	0.028	1	4	
4981.912	I	a	0.025	5	7	
4991.247	I	a	0.029	1	7	
4997.283	3	a	0.013	1	4	
4999.689	I	a	0.028	2	7	
5007.398	I	a	0.027	2	7	
5009.829	3	a	0.017	1	4	
5014.369	2	a	0.021	6	4	
5016.340	I	a	0.027	4	4	
5020.208	I	a	0.029	5	4	
5023.052	I	a	0.028	2	5	
5025.027	I	a	0.027	2	4	
5036.089	I	a	0.045	4	4	
5036.645	I	a	0.042	3	4	
5038.579	I	a	0.048	5	4	
5040.138	I	a	0.005	2	4	
5040.787	3	a	0.034	2	4	
5043.761	3	a	0.032	4	4	
5045.582	3	a	0.029	3	4	
5053.056	4	a	0.035	4	4	
5062.285	4	a	0.034	5	4	
5064.836	I	a	0.012	1	4	
5066.12	4	..	0.069	5	3	
5071.666	4	a	0.080	5	4	
5087.239	4	a	0.032	5	4	
5109.601	3	a	0.032	2	2	
5113.617	4	a	0.032	8	4	0.026	7	2	
5120.592	4	a	0.007	1	3	
5145.636	4	a	0.020	7	4	

TABLE II—Continued

A	CLASS	GROUP	ARC			SPARK			
			Δ	Mean De- viation *	No. of Plates	Δ	Mean De- viation *	No. of Plates	
5147.652	4	a	0.017	1	4	0.022	2	2	
5152.361	4	a	0.018	2	4	0.024	2	2	
5173.917	1	a	0.023	2	2	0.021	1	2	
5193.139	1	a	0.019	4	7	0.022	3	5	
5210.555	1	a	0.015	3	6	0.016	2	4	
5212.593	4	a	0.047	2	3	
5219.875	3	a	0.025	4	3	0.037	2	2	
5238.742	3	a	0.048	2	3	0.041	2	3	
5246.30	4	a	0.018	2	3	
5246.733	4	a	0.033	2	2	
5251.085	4	a	0.027	6	3	
5252.276	3	a	0.023	2	3	0.031	2	3	
5255.973	5	..	0.29	50	3	
5260.142	5	..	0.33	30	2	
5263.669	5	..	0.26	110	3	
5266.141	5	..	0.17	20	2	
5282.576	3	a	0.028	5	3	0.042	1	3	
5283.613	5	..	0.15	20	3	
5284.601	3	a	0.035	9	3	
5289.02	4	a	0.042	5	2	
5295.955	4	a	0.027	3	3	0.048	2	3	
5297.407	5	..	0.13	5	3	
5298.672	5	..	0.088	5	3	
5300.152	3	a	0.030	6	3	
5313.422	3	a	0.035	1	2	Probably Ti
5338.517	3	a	0.043	5	2	
5341.77	4	a	0.068	4	2	
5351.261	5	..	0.27	20	3	
5366.827	3	a	0.032	1	3	0.043	2	3	
5369.782	4	a	0.027	2	3	0.030	3	3	
5380.371	3	a	0.029	3	3	
5390.293	4	a	0.029	2	3	0.052	2	3	
5396.778	3	a	0.018	2	3	0.053	..	3	
5404.25	4	a	0.057	6	3	
5409.81	4	a	0.015	1	2	0.042	1	3	
5419.42	4	a	0.047	6	3	Probably Ti
5426.474	3	a	0.029	9	3	0.044	1	3	
5429.349	4	a	0.044	1	3	
5436.938	3	a	0.046	11	3	0.043	2	3	
5438.507	3	a	0.053	6	2	
5446.797	3	a	0.027	7	3	
5453.860	4	a	0.051	4	3	0.046	3	3	
5460.721	3	a	0.019	5	3	0.035	1	3	
5471.414	4	a	0.037	2	3	0.045	1	3	
5472.90	4	a	0.030	1	3	
5474.436	3	a	0.029	2	3	
5482.078	3	a	0.028	3	3	
5490.367	4	a	0.038	5	3	
5504.117	4	a	0.074	4	3	
5512.013	3	a	0.021	1	3	
5512.741	1	a	0.044	6	3	

TABLE II—Continued

A	CLASS	GROUP	ARC			SPARK			
			Δ	Mean De- viation in	No. of Plates	Δ	Mean De- viation in	No. of Plates	
5514.563	I	a	0.048	2	2	Fluting line
5514.753	I	a	0.043	2	2	
5565.700	4	a	0.040	6	8	
5597.90	3	..	0.000	0	5	
5644.365	4	a	0.033	1	5	
5648.796	5	..	0.29	40	3	
5662.374	5	..	0.23	3	3	
5675.647	5	..	0.25	20	3	
5689.694	5	..	0.25	10	3	
5702.876	5	..	0.25	20	3	
5708.46	5	..	0.24	10	4	
5712.07	5	..	0.25	20	4	
5715.308	4	a	0.048	3	5	
5727.271	3	a	0.058	4	3	
5739.698	4	a	0.042	2	5	
5740.195	3	a	0.029	2	5	
5781.130	3	a	0.046	5	5	
5823.910	3	a	0.032	1	4	
5866.675	I	a	0.034	2	5	
5880.55	3	a	0.029	3	5	
5899.518	4	a	0.034	1	5	
5903.555	3	a	0.025	2	5	
5918.773	3	a	0.022	4	6	
5922.334	4	a	0.048	4	3	
5938.035	3	a	0.038	2	3	
5941.985	4	a	0.050	4	3	
5953.386	4	a	0.020	3	3	
5966.055	4	a	0.036	4	3	
5978.768	4	a	0.018	3	3	
5996.11	3	a	0.028	1	3	
5999.920	3	a	0.050	1	3	
6064.853	3	a	0.024	4	3	Fluting line
6085.490	4	a	0.020	4	3	
6091.395	4	a	0.048	2	3	
6093.00	5	..	0.14	2	2	
6098.92	5	..	0.33	20	3	
6121.24	5	..	0.16	2	2	
6126.435	4	a	0.018	4	3	
6146.48	5	..	0.15	5	2	
6150.02	3	a	0.040	4	3	
6186.65	3	..	0.000	0	3	
6258.322	I	a	0.071	7	6	0.065	8	3	
6258.927	I	a	0.066	8	5	0.061	1	3	
6261.316	I	a	0.070	10	5	0.065	6	3	
6303.985	4	a	0.048	3	2	0.076	4	3	
6330.320	3	a	0.029	7	2	0.042	3	3	
6366.564	3	a	0.032	6	2	0.038	2	3	
6497.92	3	a	0.056	5	2	0.061	5	3	
6508.37	3	a	0.057	2	2	0.049	6	3	
6546.479	4	a	0.049	6	2	0.061	1	3	
6554.470	4	a	0.034	6	2	0.060	14	3	

TABLE II—Continued

A	CLASS	GROUP	ARC			SPARK		
			Δ	Mean De- viation ±	No. of Plates	Δ	Mean De- viation ±	No. of Plates
6556.308	4	a	0.049	0	2	0.059	2	3
6599.353	3	a	0.035	15	2	0.052	1	3
6719.90	4	a	0.058	3	2
6861.770	4	a	0.084	2	2

strengthened at low temperatures) being symmetrical and, though broad, fairly well defined as a rule.

3. Except in the ultra-violet the enhanced lines of titanium are always bright in the arc under a pressure of 9 atmospheres. In the titanium spark at the same pressure they are usually faintly reversed. This agrees with Duffield's hypothesis that conditions in the electric spark are more favorable to the production of reversals than they are in the arc.

4. The number of reversed lines at a pressure of 9 atmospheres is somewhat less than that found by Duffield¹ for pressures of 20 to 25 atmospheres. This agrees with the conclusion of Humphreys that in the case of iron, for moderate pressures at least, the number of reversals increases with the pressure.

Some additional characteristics of certain of the lines will be referred to in the course of the discussion of the displacements.

Since our work upon the iron spectrum has been limited to the arc, and all of the photographs have been taken at a pressure of 9 atmospheres, while the results for titanium include both arc and spark, and for some of the lines a variety of pressures as well, we shall discuss the displacements for the two elements separately.

IRON

In the following table we have compared our results with the most recent values obtained by Humphreys and by Duffield² for such lines as are common to all three sets of observers. To reduce to a value of 9 atmospheres total pressure, Duffield's values for

¹ *Phil. Trans.*, A 208, 111, 1908.

² *Jahrbuch der Radioaktivität und Elektronik*, 5, 324, 1908.

11 atmospheres are reduced by one-fifth, while Humphreys' values for 42 atmospheres are divided by the quantity 5.1. Series B in Duffield's investigation has been used, as this is considered preferable by the author.

λ	Humphreys	Duffield	Gale and Adams
4132.235.....	0.020	0.021	0.024
4144.038.....	.023	.021	.029
4202.198.....	.014	.017	.025
4233.772.....	.047	.144	.090
4250.945.....	.017	.018	.022
4260.040.....	.048	.051	.051
4271.934.....	.016	.017	.022
4282.505.....	.009	.018	.021
4294.301.....	.017	.019	.029
4308.081.....	.018	.019	.021
4315.262.....	.007	.013	.019
4325.939.....	.019	.026	.020
4337.216.....	.018	.034	.027
4352.908.....	.010	.020	.017
4369.941.....	.011	.026	.023
4376.107.....	.008	.017	.018
4404.927.....	.022	.043	.021
4415.293.....	.017	.033	.018
4422.741.....	.013	.022	.018
4427.482.....	.011	.018	.017
4430.785.....	.037	.057	.048
4442.510.....	.037	.057	.053
4443.365.....	.012	.022	.019
4447.892.....	.035	.062	.051
4454.552.....	.016	.018	.023
4459.301.....	.031	.063	.051
4461.818.....	.012	.018	.015
4466.727.....	.011	.021	.018
4476.185.....	.014	.021	.021
4494.738.....	.040	.058	.053
4531.327.....	0.015	0.026	0.029

If we omit the line λ 4233.772, which is unsymmetrical and extremely difficult of measurement, a comparison of the remaining 30 lines gives the following mean values:

Humphreys.....	0.019
Duffield.....	0.029
Gale and Adams.....	0.027

The agreement of our results with those of Duffield is close, but the average value found for the observations of Humphreys is rather surprisingly small. This may be due in part to the fact that the linear relationship between displacement and pressure fails to

hold at high pressures, although this seems improbable in view of the very close accordance found by other observers for several elements and shown by our own measures upon the titanium spectrum. A few of these lines measured by Humphreys in a previous investigation at lower pressures give distinctly larger values for the displacements, and these agree closely with those obtained by Duffield and ourselves.

In any discussion of the effect of pressure upon the lines of the spectrum there is a natural tendency to institute a comparison with the other two causes which are known to affect different lines of a spectrum differently. The first of these is variation of temperature; the second is the presence of a magnetic field.

The lines of iron which are strengthened relatively at low temperatures and which are usually referred to as "flame" lines are well known.¹ The most prominent of these lines for which we have determined the pressure displacements are the following:

λ	Δ	λ	Δ
3680.069.....	0.007	4427.482.....	0.017
3705.708.....	.007	4461.818.....	.015
3720.084.....	.014	4489.911.....	.015
3722.600.....	.010	5227.362.....	.031
3733.469.....	.007	5269.723.....	.027
3737.281.....	.016	5328.236.....	.029
3745.717.....	.008	5333.089.....	.029
3746.058.....	.008	5341.213.....	.028
3748.408.....	.010	5371.734.....	.029
3886.434.....	.011	5397.344.....	.029
3895.803.....	.011	5405.989.....	.027
3899.850.....	.012	5429.911.....	.029
3906.628.....	.011	5434.740.....	.027
3920.410.....	.010	5447.130.....	.031
3923.054.....	.011	5455.834.....	.029
3928.075.....	.012	5476.778.....	.029
3930.450.....	.013	5497.735.....	.030
4291.630.....	.014	5501.685.....	.030
4376.107.....	0.018	5507.000.....	0.031

With the exception of the two lines λ 4291.630 and λ 4489.911, which are faint, all of these lines are suitable for measurement, being fairly sharp under pressure, and the precision of the results

¹ De Wetteville, *Phil. Trans.*, A 204, 139, 1904; Adams, *Contributions from the Mount Wilson Solar Observatory*, No. 40; *Astrophysical Journal*, 30, 86, 1909.

is high, especially for the more refrangible lines. Except in the violet region there are no reversed lines among them.

It is apparent at a glance that the displacements given by these lines are decidedly smaller than those of the other lines in the same region. The average displacement of the 17 flame lines in the ultra-violet region is about 0.010 Ångström, while the average for 27 other lines in the same region is 0.015. In the green region the difference is even more striking, although here it is not possible to compare the flame lines directly with the other lines in the same region owing to the fact that the latter appear to belong to a totally distinct group as regards displacements, giving values about four times as great as the flame lines. We can, however, compute a value for this region from the value in the blue region, assuming the law of variation according to the cube of the wave-length which seems to hold closely for these lines. In this way we obtain 0.044 as against 0.029 for the flame lines. An interesting characteristic of the flame lines is the close agreement of the displacements of the different lines in the same part of the spectrum. This fact taken in connection with their behavior at reduced temperatures makes it very probable that they form members of a single group. An examination of the results obtained by King¹ for the electric-furnace spectra under pressure shows that the flame lines give distinctly lower displacements than the other lines in this source as well. It is worthy of note that in an investigation of the displacement of the spectrum lines at the sun's limb² it was found that the flame lines in general gave smaller values than the other lines of the same element.

A study of the relationship between displacements under pressure and separations in a magnetic field has been made by King³ for a large number of iron lines and a considerable number of titanium and chromium lines. For the purpose of comparing the displacements and separations he has formed the quotients of all the lines for

¹ *Contributions from the Mount Wilson Solar Observatory*, No. 53; *Astrophysical Journal*, **34**, 37, 1911.

² *Contributions from the Mount Wilson Solar Observatory*, No. 43; *Astrophysical Journal*, **31**, 30, 1910.

³ *Contributions from the Mount Wilson Solar Observatory*, No. 46; *Astrophysical Journal*, **31**, 433, 1910.

which the data are available, and from a comparison of these quotients has concluded that no direct relationship exists between the two quantities, although for the average of large groups of lines the effects are in the same direction.

It is hardly possible in this place to repeat the calculations with the use of the values of the displacements given in this investigation. A few results, however, which can readily be confirmed are as follows:

1. The use of the pressure displacements given here reduces greatly a considerable number of the largest differences found by King. As examples we may refer to λ 3920.410, λ 3923.054, λ 3928.075, λ 3977.891, λ 4315.262, and λ 4376.107, all of which are brought into much closer agreement with the other lines.

2. A majority of the serious discordances between pressure displacements and magnetic separations are in the cases of lines which are found to be complex in the magnetic field. Apart from the uncertainty of measurement of the separations of many of these lines, it is improbable on the basis of any of the theories of the Zeeman effect that there would be a direct relationship between separations and pressure displacements for such lines except perhaps for those of exactly the same type. We should expect rather that these lines would be greatly widened under pressure. It is interesting to note in this connection that nearly all of the strong flame lines in the yellow portion of the spectrum are complex in the magnetic field, while many of the other lines are triplets. The former lines show some of the most serious discrepancies between separation and displacement that are found in the entire list. Similarly in the violet part of the spectrum we may refer to the complex lines λ 4191.595 and λ 4233.722, which show large differences.

3. Since the pressure displacements for iron vary as the cube of the wave-length and the magnetic separations as the square, it is necessary in comparing the results to multiply the separations by the ratio of wave-lengths. This is found to bring the results in the less refrangible region of the spectrum into much closer agreement with those in the violet.

4. It seems probable from the fact that the lines of iron appear to divide themselves into groups, both as regards pressure displace-

ments and magnetic separations, that the ratios of the two quantities may by no means be the same for different groups, although constant within any given group for the same types of lines.

5. The significance of the agreement of very large and very small displacements and separations for certain lines seems to us of great importance. Of the former type we may mention the triplets λ 4210.494, λ 4407.871, λ 4430.785, and λ 4878.407. In the red we may refer to the triplet λ 6302.709, which is not measurable under pressure but has an immense displacement. The evidence from the behavior of such a group of lines as that between λ 4430 and λ 4461, for which displacements and separations unmistakably rise and fall together, is especially important.

6. The number of very marked discrepancies between size of displacement and separation among the triplets is not large, but a few of them are very important. A single most striking case is λ 6173.553 which gives an average pressure displacement but an exceedingly wide separation. It is a wide triplet in sun-spots. Another case in which the discordance is not so great is λ 4071.908.

7. Three lines which show no measurable separation in a magnetic field have been measured under pressure. Two of them, λ 3746.058 and λ 5434.740, give small displacements under pressure, while the third line, λ 3767.341, gives an average value. All three are rather narrow under pressure.

8. Attention should be called to the extreme sensitiveness of these comparisons to errors of observation. To illustrate: if we assume a magnetic separation of 0.350 Ångström for a given line and a pressure displacement of 0.020 Ångström, which is not far from an average value for the violet, we obtain the quotient 17.5. For the very best lines under pressure it is difficult to obtain probable errors of less than ± 0.002 , which would produce a variation in the quotient of from 16 to 19. For many lines the probable error is several times this amount. Furthermore, our experience with titanium at different pressures indicates that the probable error increases almost in proportion to the pressure, so that the use of high pressures brings little gain on account of the deterioration of the lines. On the side of the magnetic separations errors of measurement also influence the comparisons, so that a very con-

siderable range in the results is to be expected from these sources. The type of separation also is very often uncertain, as is shown by the numerous changes in classification made by the same observer when different analyzing apparatus is used.

In view of these results it seems to us that the balance of evidence is somewhat in favor of a direct relationship between pressure displacements and separations in the magnetic field for lines which are of the same type. For lines of complex type and for lines which under pressure become extremely unsymmetrical the values are discordant, a result which is not surprising.

VARIATION OF DISPLACEMENT WITH WAVE-LENGTH

As soon as the measures of the displacements for all the iron lines were completed we plotted the results upon a large scale, using wave-lengths as abscissas and displacements as ordinates. A similar chart is shown in Fig. 1. The chart at once shows that certain groups of lines for which the average displacements differ widely apparently belong together. Furthermore, a comparison of the displacements of the flame lines with those of the other lines indicates clearly that such lines are to be considered as a separate group. In this way four groups have been found, and the lines included in each group are indicated in Table I by the letters *a*, *b*, *c*, and *d*. Group *a* includes all of the flame lines and two or three additional lines in the yellow portion of the spectrum, which may be flame lines but for which observations are lacking. Group *b* is a large one and includes all lines of small displacements which are not included in group *a*. It may well be complex in nature but in the absence of criteria for separating it into smaller groups we are obliged to consider it as a unit. Group *c* consists of lines showing much larger displacements than those of group *b*. It contains two fairly distinct clusters of lines, one in the violet and one in the blue green. The lines are all bright under pressure and especially in the green region unsymmetrical and difficult of measurement. Group *d* is made up of a very few lines in the violet, a fair-sized group in the greenish yellow, and a small number in the red, all of which show immense displacements. The lines are bright and widened enormously to the red, the wings extending sometimes from 5 to 10

Ångström units. The precision of measurement upon these lines necessarily is very low, in some cases the determination amounting to little more than an estimate of the maximum within the broad band.

The average values of the displacements and of the corresponding wave-lengths for the lines forming these groups provide us the

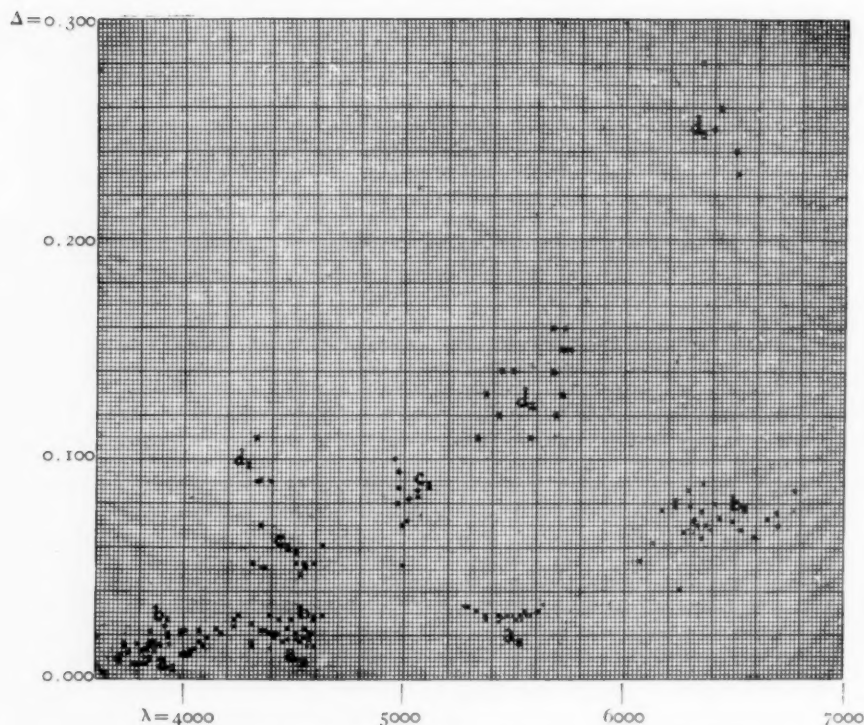


FIG. 1.—Displacement of lines of the iron arc at 8 atmospheres pressure.

material for a discussion of the variation of displacement with wave-length. In the following table the results are collected for the four groups. The second column gives the mean of the wave-lengths of the lines for which the mean displacement is formed. The third column contains the mean displacements expressed in Ångström units. The fourth column gives the number of lines for each portion of the group. It is evident from a simple inspection of the

results that the increase of displacement toward longer wave-lengths is much more than would be given by a law based on the first power of the wave-length. In the last two columns of the table are given the residuals for two hypotheses: first, that the displacement varies as the square of the wave-length; second, that it varies as the cube of the wave-length.¹ The reductions have been made by least squares, with weights assigned according to the number of lines. The fourth group is of course of very low weight compared with the others.

GROUP	MEAN λ	MEAN Δ	NO. LINES	RESIDUALS (OBS. - COMP.)	
				$\Delta = \left(\frac{\lambda}{\lambda_0}\right)^2 k$	$\Delta = \left(\frac{\lambda}{\lambda_0}\right)^3 k$
a.....	3813	0.0105	17	-0.0032	+0.0002
	4400	.0158	5	-0.0025	-0.0001
	5398	.0292	19	+0.0017	-0.0001
b.....	3791	.0164	27	-0.0072	+0.0007
	4287	.0219	29	-0.0083	-0.0008
	6292	.0719	27	+0.0069	+0.0001
c.....	4395	.0547	11	-0.0058	-0.0020
	4902	.0803	10	+0.0051	+0.0016
d.....	4249	.09	4	-0.01	+0.02
	5498	.14	15	-0.02	-0.01
	6339	0.25	5	+0.04	+0.01

These results are also shown graphically in Fig. 2. The points correspond to the observed, and the curves to the computed values, assuming the law of the cube of the wave-length.

It is clear from the results that the displacements for all of the groups of lines are represented with a surprisingly high degree of accuracy by a law which involves the third power of the wave-length, and in view of the great range of wave-length covered by the observations this may probably with safety be assumed to be true of the entire iron spectrum. In some recent work by Rossi upon the arc spectrum of vanadium,² he concludes from his observa-

¹ Strictly speaking the means of the second and third powers of the individual wave-lengths should be used instead of the second and third powers of the means of the wave-lengths, but the difference is negligible for the purposes of this comparison.

² *Astrophysical Journal*, 34, 21, 1911.

tions that "the displacement seems to be roughly proportional to the square or a higher power of the wave-length," and Duffield in his investigation of the iron spectrum found that the linear relation-

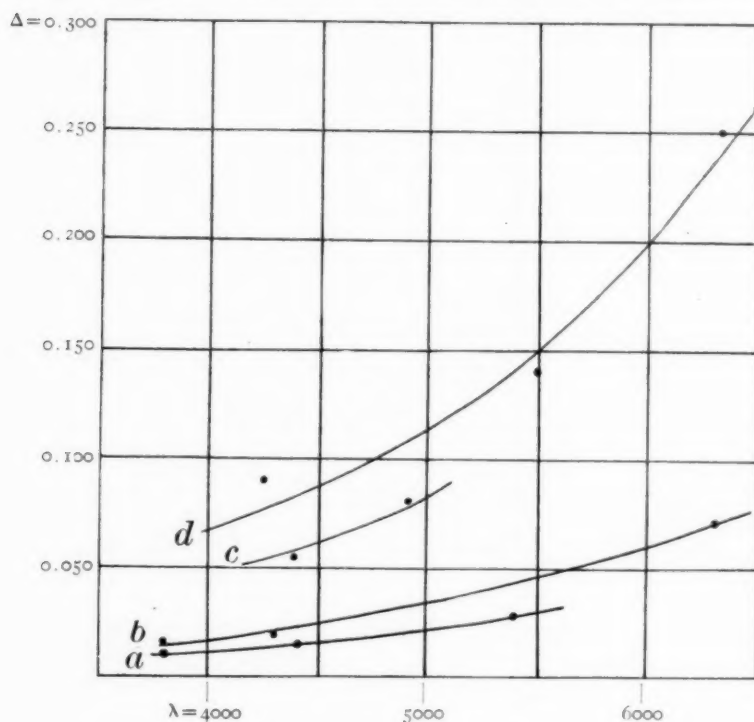


FIG. 2.—Mean displacement and mean wave-length of iron groups. Curves represent computed, points observed, values.

ship would not hold. Similarly Duffield in his discussion of the effect of pressure upon the arc spectra of silver and gold writes:¹

It seems at least certain that the displacement varies with a higher power of the wave-length than the first upon which it was previously believed to depend. The results of the present investigation favor a dependence upon the third power of the wave-length, and this agrees with some theoretical deductions made by Dr. O. W. Richardson.²

From the results of his investigation of the iron spectrum Duffield concluded that there are three groups of lines for which

¹ *Phil. Trans.*, A 211, 66, 1911.

² *Phil. Mag.*, 14, 557, 1907.

the displacements are approximately in the ratio of 1:2:4. A comparison with his results shows that so far as the same lines have been measured these groups are identical with our groups *b*, *c*, and *d*, except for the fact that we have included the flame lines in a separate group. In addition, the line λ 4260.640 which Duffield places in group 3 is placed by us in group *b*. It is a very unsymmetrically reversed line and subject to great variations in appearance under pressure. If we compare the violet portions of these groups, reducing to wave-length λ 4287, we obtain the ratios:

<i>b</i>	<i>c</i>	<i>d</i>
1	2.3	4.5

Similarly Duffield has for his groups:

I	II	III
1	2.0	4.5

The agreement between the two sets of results is close and in view of the accuracy of the results the departure from the whole numbers seems to be sufficiently great to make the integer relationship improbable. If we include the group of flame lines we obtain the ratio 0.67 between groups *b* and *a*; or, if we reduce all values to group *a* we find the relationship:

<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
1	1.5	3.4	6.6

If the first two groups are united we have the ratios

1	2.5	4.9
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It seems to us therefore improbable that the displacements of the different groups of iron lines bear ratios to one another which are proportional to small integers.

TITANIUM

Two previous investigations of the arc spectrum of titanium under pressure are available. The first of these, by Humphreys,¹ was carried on at pressures between 42 and 101 atmospheres, and the second, by Rossi,² at pressures between 16 and 101 atmospheres. Unfortunately very few lines are common to all three series of

¹ *Astrophysical Journal*, 26, 18, 1907.

² *Proc. Roy. Soc., A* 83, 414, 1910.

observations. A comparison with the results of Humphreys shows that our values are larger by about the same amount as in the case of iron. The average of the lines agrees well with that of Rossi, although there are some large individual discrepancies.

One of the features which stands out most prominently in these results is the behavior of the enhanced lines. A large majority of them show displacements decidedly larger than those of the great proportion of arc lines in the vicinity, in some parts of the spectrum the average difference amounting to as much as 50 per cent. The effect, however, is not true of all enhanced lines, such lines, for example, as $\lambda 4338.084$ and $\lambda 4443.976$ showing small values as compared with neighboring arc lines. Nearly all of the enhanced lines present in the arc spectrum are bright at a pressure of 9 atmospheres, and being rather broad and diffuse are difficult of measurement. We have for this reason given especial attention to them, particularly in the region $\lambda 4300$ to $\lambda 4600$, and few of the values are based upon the measurement of less than four plates. The exceptional behavior of most of these lines is fully confirmed by the spark results, and is of marked interest in view of their importance in solar and stellar spectroscopy.

An inspection of the results given in Table II shows that the intermixture of the groups in the spectrum of titanium, if such exist, must be most complicated, and the simple expedient of plotting the displacements graphically, which proved so useful in separating the groups of lines in the iron spectrum, has been of little value. In the violet part of the spectrum nearly all of the lines as far as $\lambda 4080$ are reversed and show small displacements. At this point, however, begins a series of unreversed lines extending to $\lambda 4285$, which show relatively large displacements. Beyond $\lambda 4290$ both reversed and unreversed lines occur and the average displacement is less than in the region $\lambda 4080$ - $\lambda 4290$. In the green, yellow, and red portions of the spectrum the number of reversed lines falls off steadily but the displacements are found to range between very small and very large values, although showing a marked increase on the average. There is probably little doubt that the collection of lines showing displacements of some 0.2 Ångström in the green and yellow parts of the spectrum form parts of a group

similar to group *d* in the iron spectrum. The violet members of this group may perhaps be λ 4318 and λ 4321, which have displacements of about 0.1 Ångström. These lines are all unreversed and immensely widened toward the red, and very similar in appearance to the iron lines of group *d*.

A comparison of the titanium lines of group *a* with those which are affected in sun-spots shows that the lines which are most strengthened in spots as a rule show small displacements under pressure, although the agreement is by no means perfect. The fact that the number of low-temperature lines increases very rapidly in the less refrangible parts of the spectrum may account, perhaps, for the lower average for the displacements of the titanium lines in these regions.

In view of the impossibility of separating the groups in the titanium spectrum it is perhaps not surprising that a general comparison of our pressure displacements with the separations in a magnetic field gives little evidence of any direct relationship between these quantities. As in the case of iron, the use of these displacements instead of those of Humphreys reduces in a marked degree the number of large discordances for lines which are simple triplets in the magnetic field. Such lines, however, as λ 4841.074, λ 5040.138, and λ 5120.592, which show very small pressure displacements but average separations, must necessarily form part of a separate group and a much larger number of groups than in the case of iron must be assumed in order to account for the wide variations observed. The question must be considered an open one.

The relationship between displacement and wave-length in the case of titanium clearly is complicated by the presence of the different groups of lines. A rather surprising result is given if we form simple means of the displacements for definite regions of the spectrum. Omitting the enhanced lines and some lines with very large displacements already referred to, the remainder (indicated by *a* in Table II) give the average values on the following page.

In the last two columns are given the residuals, assuming: first, that the displacement varies as the square of the wave-length; second, that it varies as the third power of the wave-length. The results show clearly that the law of the square of the wave-length

satisfies the observations the more closely. In the iron spectrum, on the other hand, the law was found to be the third power of the wave-length. As already indicated, the relatively large value of the

REGION	MEAN λ	MEAN Δ	NO. LINES	RESIDUALS (OBS. - COMP.)	
				$\Delta = \left(\frac{\lambda}{\lambda_0}\right)^2 k$	$\Delta = \left(\frac{\lambda}{\lambda_0}\right)^3 k$
3700-4700...	4288	0.0250	115	+0.0016	+0.0064
4700-5700...	5142	0.0344	100	+0.0008	+0.0023
5700-6900...	6127	0.0439	38	-0.0038	-0.0102

average displacement in the violet is due to a considerable extent to the group of unreversed lines of large shifts between λ 4080 and λ 4285. If these were omitted, however, and only reversed lines considered throughout the entire spectrum, the difficulty would remain that the reversed lines in the region λ 4400 to λ 4600 give a value of the displacement quite as large on the average as do the reversed lines in the region λ 4800 to λ 5200. Accordingly it seems impossible without separating the lines in a very arbitrary way to obtain a series of average displacements which will harmonize with a law based upon the third power of the wave-length. It is sufficient to state that for the general averages of large numbers of lines taken throughout the spectrum the law of the square of the wave-length seems to hold closely, and to leave further discussion to a time when it is possible to distinguish groups in the titanium spectrum.

It may be of interest in this connection to call attention to some other results which suggest the possibility that the law of variation of displacement with wave-length may differ between titanium and iron. At the sun's limb the lines of nearly all the elements are shifted slightly toward the red relative to their positions in the spectrum of the center of the sun,¹ a result due probably to the greater influence of the lower strata of gas in the production of the lines in the limb spectrum. A study of the displacements of a large number of lines of different elements by Adams² shows that in the case of iron the change of displacement with wave-length is not

¹ Halm, *Astronomische Nachrichten*, **173**, 273, 1907.

² *Contributions from the Mount Wilson Solar Observatory*, No. 43; *Astrophysical Journal*, **31**, 30, 1910.

far from proportional to the square of the wave-length, while in the case of titanium it is much less, being more nearly proportional to the first power. In other words, if two groups of iron and titanium lines had the same average displacement in one part of the spectrum λ_0 , in any other part λ the average displacements would bear the relationship

$$\Delta_{Fe} = \left(\frac{\lambda}{\lambda_0} \right) \Delta_{Ti}.$$

This is the same result as that which we have found for iron and titanium under pressure. Conditions in the sun are, of course, very complicated, and the displacement of each line depends upon its level, the amount of scattering and absorption of light in different portions of the spectrum, the thickness of the absorbing vapor, and many other factors as well. For these reasons we might expect that the law of variation of displacement with wave-length would differ from that found in laboratory spectra. Unless we assume a radically different level for iron and titanium in the solar atmosphere, however, we should expect the two elements to bear the same relationship to one another in the sun as that which they bear in the laboratory, and this appears to be the case.

Another result which may have a bearing upon the question of a difference in the laws of variation of displacement with wave-length for different elements is contained in a few measurements we have made upon some series lines in the spectrum of calcium at a pressure of 9 atmospheres (total). The second subordinate series of calcium contains a triplet in the violet beginning at λ 3949 and a triplet in the red at λ 6102. The red lines are fairly well measurable, but the violet lines are extremely poor in quality. We have, however, succeeded in obtaining a few measures upon two of them. The results follow:

λ	Δ	No. Plates
3957.177.....	0.081	3
3973.804.....	.085	3
6102.937.....	.139	2
6122.434.....	.136	2
6162.390.....	0.137	2

The close agreement of the separate lines is largely accidental, as their quality is not such as to warrant it. Averaging the two sets of lines we find:

λ	Δ	Obs.—Comp.
3965.....	0.083	-0.003
6129.....	0.137	+0.004

It is clear that the relationship between displacement and wave-length for these results is very nearly a linear one. The last column gives the residuals on such a hypothesis. Since these are series lines there can be no doubt of their connection with one another, and although the accuracy of measurement is low, it is hardly probable that the results can be in error sufficiently to admit of a law containing the second power of the wave-length, much less the third.

Although it is not possible to consider differences in the law of change of displacement with wave-length for different elements as established by these results, there is perhaps sufficient evidence to warrant a reference to the chemical relationship of the three elements. Calcium, titanium, and iron appear in the second, fourth, and eighth groups of the Mendelëeff table, with atomic weights of 40, 48, and 56, and atomic volumes of 25, 13, and 7, respectively. It is perhaps conceivable that the law which connects pressure displacement with wave-length may be different for the different groups of the Mendelëeff table.

The principal question remaining for consideration in these results is that of a possible difference between the displacements of arc and spark lines at the same pressure. The quality of the spark lines under pressure unfortunately is as a rule by no means equal to that of the corresponding arc lines, the reversals being much wider and more diffuse and the unreversed lines often less symmetrical. An inspection of the tables shows a marked tendency toward higher values for the spark displacements. Probably the most accurate results may be obtained from a comparison of a list of 20 lines, none of which is enhanced, between λ 4427 and λ 4555, employed in an investigation of the variation of displacement with amount of pressure and given in Table III. These lines have been measured upon an exceptionally large number of spark photographs

so that the results obtained should be reasonably comparable in accuracy with the arc values. Taking the means of the displacements of these 20 lines we find the values:

$$\Delta_{\text{spark}} = 0.037, \quad \Delta_{\text{arc}} = 0.030; \quad \text{or } \Delta_{\text{spark}} - \Delta_{\text{arc}} = 0.007 \text{ Ångström.}$$

Very nearly the same value is given by a comparison of the lines throughout the entire spectrum. It seems hardly probable that a difference of this magnitude can be due to uncertainty of measurement, and the fact that arc and spark photographs were taken under exactly the same conditions, sometimes alternating with one another, reduces the probability of instrumental source of error. Since the reversals of the spark lines are broader than those of the arc it is possible that the larger displacements in the spark are due to an average widening of the reversals toward the red more than toward the violet, and as the amount of this effect would no doubt be peculiar to each line it might well account for the large variations between separate lines. The reversals in most cases, however, appear symmetrical upon the photographs.

In the case of the enhanced lines the differences between arc and spark displacements are even more marked. *The average difference for all of the enhanced lines which occur in both lists is 0.014 Ångström*, or about twice that found for the other lines. The values are

$$\Delta_{\text{spark}} = 0.051; \quad \Delta_{\text{arc}} = 0.037.$$

The enhanced lines in the spark spectrum are exceedingly difficult of measurement, but there probably can be little question of the existence of a difference of considerable size. The percentage of increase of the spark values over those of the arc also is greater than for the other lines.

The important question whether the relationship between displacement and amount of pressure is strictly linear has been considered by all who have carried on pressure investigations. Humphreys, Duffield, and Rossi have all shown that over a wide range of pressures, for the most part above 15 atmospheres, the displacements are directly proportional to pressure within the accuracy of the observations, although Duffield found some contradictory results between 15 and 25 atmospheres. In order to make an accurate test of the law at low pressures we have taken a special

series of photographs of the titanium arc in the region λ 4300– λ 4600 at pressures ranging from 2 atmospheres to 16 atmospheres above atmospheric pressure. A few photographs in a partial vacuum have been obtained as well. We have selected a list of 20 lines, all of which are reversed and well adapted for measurement on these photographs, and have used the averages of the displacements of these 20 lines at the various pressures for purposes of comparison. The results for each line together with the mean deviations are given in Table III.

TABLE III

λ	2 ATMOS. 6 PLATES		4 ATMOS. 4 PLATES		6 ATMOS. 4 PLATES		8 ATMOS. 10 PLATES		12 ATMOS. 4 PLATES		16 ATMOS. 4 PLATES	
	Δ	Mean Dev.	Δ	Mean Dev.	Δ	Mean Dev.	Δ	Mean Dev.	Δ	Mean Dev.	Δ	Mean Dev.
4427.266	4	1	9	2	15	1	17	3	30	2	41	2
4449.313	8	2	15	1	24	2	29	4	49	1	69	2
4451.087	8	1	16	3	25	3	28	2	48	3	73	3
4453.486	12	1	23	2	33	1	40	4	62	6	87	7
4455.485	12	1	24	3	34	3	41	2	64	3	92	6
4457.600	10	1	23	3	33	2	39	3	63	1	86	3
4465.975	8	2	15	1	21	2	25	2	42	1	51	5
4471.408	7	1	12	1	19	2	23	3	44	1	53	6
4481.438	6	1	13	1	19	2	23	2	43	2	59	3
4512.906	9	1	15	2	25	2	30	2	50	3	68	3
4518.198	8	1	15	2	25	1	30	2	45	2	68	5
4522.974	9	1	16	3	25	1	31	3	52	2	71	6
4527.490	9	1	17	2	26	1	32	4	48	1	71	2
4533.419	8	1	17	2	24	1	31	2	49	4	66	1
4534.953	12	3	13	1	25	1	34	3	49	1	70	2
4535.741	8	1	15	1	24	2	29	3	51	1	66	3
4544.864	9	1	16	4	26	1	31	2	50	3	68	2
4548.938	8	1	17	2	25	3	31	2	51	3	70	5
4552.632	8	1	17	2	24	2	30	3	50	1	70	6
4555.662	10	1	17	3	28	2	31	2	55	3	75	6
Mean..	8.6	1	16.2	2	25.0	2	30.3	3	49.8	2	68.7	4

If we assume the linear relationship and reduce the mean values by a least-squares solution we obtain the following residuals:

	Obs. – Comp.	Δ per Atmos.
2 atmos.....	+0.0005	0.0043
4 atmos.....	–0.0003	.0040
6 atmos.....	+0.0003	.0042
8 atmos.....	–0.0026	.0038
12 atmos.....	+0.0004	.0042
16 atmos.....	+0.0028	0.0043

The largest deviation from the linear law, accordingly, at any of these pressures is found to be only 0.0028 Ångström. The displacement per atmosphere is given in the last column of the table. The average of these values is 0.0041 Ångström. Similarly for the average displacement between 15 and 100 atmospheres for 16 of the same lines Rossi finds 0.0045. The close agreement of these results makes it almost certain that the linear law of the variation of displacement with pressure holds perfectly between atmospheric pres-

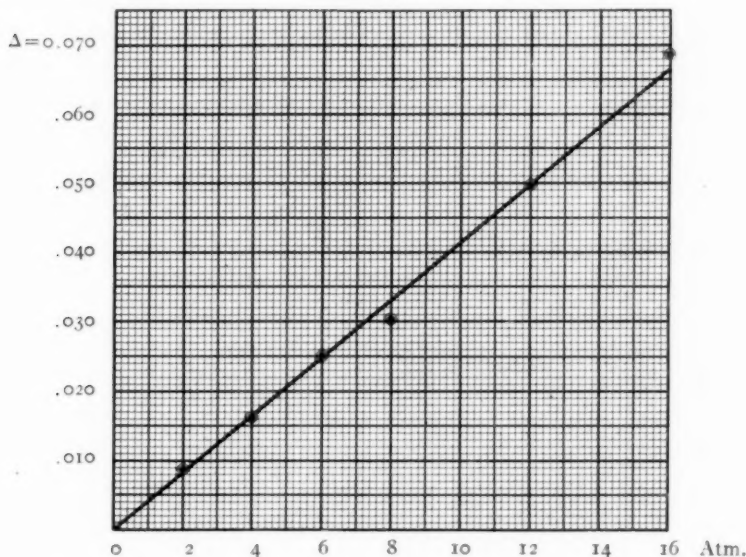


FIG. 3.—Mean displacement of 20 selected titanium lines at different pressures.

sure and 101 atmospheres. The results are shown graphically in Fig. 3.

In the course of the investigation a number of photographs were made of the titanium arc in an atmosphere of illuminating gas. The arc under such conditions burns very poorly, and it is necessary to employ a very short gap and secure the exposure from a series of intermittent flashes rather than a continuous flame as in air or carbon dioxide. The photographs were all made at a pressure of 4 atmospheres. It is well known that an atmosphere of hydrogen has the effect of strengthening the enhanced lines at atmospheric

pressure and the same is found to be true at a pressure of 4 atmospheres. We have measured on these photographs most of the arc lines in the selected list of 20 lines and also all well-measurable enhanced lines in the same region. The appearance of the lines does not differ greatly from that in an atmosphere of carbon dioxide except for the greater relative strength of the enhanced lines. The arc lines measured are all reversed; the enhanced lines unreversed. The results are shown in Table IV, compared with the corresponding values for the same pressure in an atmosphere of carbon dioxide. The displacements are in thousandths of an Ångström.

TABLE IV

A	4 Atmos. <i>H</i>	No. Plates	4 Atmos. <i>CO</i> ₂	No. Plates	Difference $\Delta_H - \Delta_{CO_2}$	
4427.266	11	5	9	4	+ 2	
4443.976	9	6	7	5	+ 2	Enhanced line
4449.313	15	2	15	4	0	
4451.087	13	2	16	4	- 3	
4453.486	23	2	24	4	- 1	
4455.485	22	5	24	4	- 2	
4457.600	24	5	23	4	+ 1	
4465.975	15	5	14	4	+ 1	
4468.663	31	6	26	5	+ 5	Enhanced line
4471.408	10	2	11	4	- 1	
4481.438	10	2	13	4	- 3	
4501.445	34	6	27	5	+ 7	Enhanced line
4512.906	14	5	15	4	- 1	
4518.198	17	2	15	4	+ 2	
4522.974	14	2	16	4	- 2	
4527.490	17	5	17	4	0	
4534.139	24	6	20	5	+ 4	Enhanced line
4544.864	17	5	16	4	+ 1	
4548.938	14	2	17	4	- 3	
4549.808	41	6	31	5	+ 10	Enhanced line
4555.662	15	4	17	4	- 2	
4563.939	29	6	22	5	+ 7	Enhanced line
4572.156	41	5	33	5	+ 8	Enhanced line

The interesting result is brought out by these measures that while the 16 arc lines in the list give practically identical values in hydrogen and carbon dioxide, the enhanced lines show distinctly larger values in hydrogen. The average values for $\Delta_H - \Delta_{CO_2}$ are:

$$\begin{aligned} 16 \text{ arc lines} & \dots\dots\dots -0.0007 \\ 7 \text{ enhanced lines} & \dots\dots\dots +0.0061 \end{aligned}$$

Moreover, the increase of displacement in hydrogen for an enhanced

line seems to be a direct function of the normal displacement of the line, amounting to about 25 per cent at 4 atmospheres. Thus the line λ 4443.976 which is displaced only 0.007 in CO_2 is displaced 0.009 in H , while λ 4501.445 which is displaced 0.027 in CO_2 is displaced 0.034 in H , the same ratio holding for both. In view of the quality of the lines and the accuracy of the measures it seems to us that this result is almost certainly genuine and that the nature of the surrounding gas exerts an influence upon the displacements of the enhanced lines. It appears probable, therefore, that a change from a carbon dioxide to a hydrogen (illuminating gas) atmosphere affects not only the intensities but the displacements of the enhanced lines in the same way as does a change from arc to spark.

We have already referred to some of the more important applications of the results of this investigation to solar spectroscopy. The fact that the enhanced lines show materially larger displacements both at the sun's limb and under pressure than do the other lines strengthens greatly the view that pressure is the effective agent in producing the solar displacements. As was pointed out previously, evidence in the same direction is afforded by the two facts that both in the arc under pressure and at the sun's limb the low-temperature lines give small displacements, and that both in arc and sun the ratio of the laws of change of displacement with wave-length for iron and titanium is the same. We have referred briefly in an earlier communication¹ to the possible bearing upon the character of the spectrum of the solar chromosphere of the fact that at moderate pressures the enhanced lines remain bright while a majority of the other lines are reversed. A result which probably has an application in the same direction but especially to the spectrum of the upper chromosphere and of prominences is furnished by our photographs of the titanium arc at reduced pressure. These show a marked increase of relative intensity for the enhanced lines as compared with that which they have at atmospheric pressure.² At the very low pressures of the upper portions of the solar atmosphere this fact may well account for the prominence of the enhanced

¹ *Science*, **32**, 881, 1910.

² A similar result has been found by Barnes for *Al*, *Mg*, and *Cu*, *Astrophysical Journal*, **34**, 159, 1911.

lines in the flash spectrum. The change of intensities of the enhanced lines at reduced pressure is well shown in Plate III.

SUMMARY

An investigation of the arc spectrum of iron at a pressure of 9 atmospheres and of the arc and spark spectra of titanium at pressures of from a partial vacuum to 17 atmospheres over a range of wave-length from λ 3600 to λ 6800 furnishes the following results:

1. Reversal is a function of wave-length, being most frequent in the more refrangible part of the spectrum and becoming less so toward longer wave-lengths.

2. With reduction of pressure below one atmosphere the enhanced lines in the spectrum of titanium become relatively stronger.

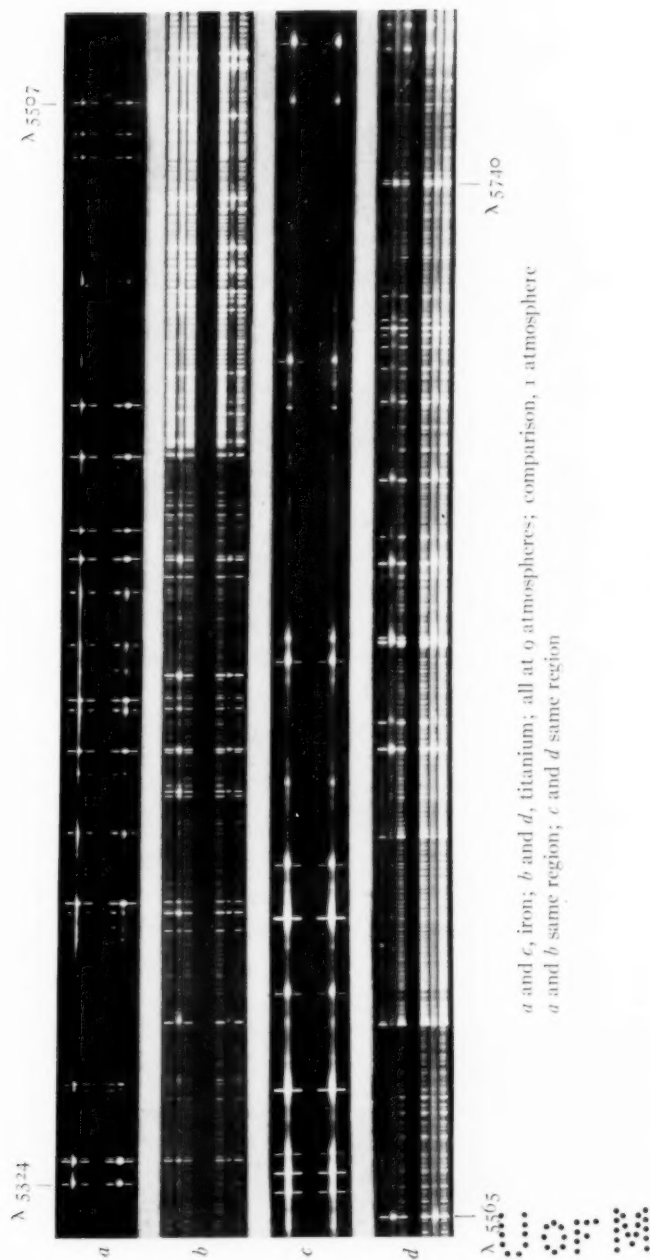
3. The low-temperature lines of iron appear to form a distinct group and have small displacements under pressure.

4. The other lines of iron may be divided into three groups for which the displacements bear the approximate ratios 1 : 2.3 : 4.5. If the flame lines are taken as a separate group the ratios are 1 : 1.5 : 3.4 : 6.6.

5. There appears to be some evidence in favor of a direct relationship between pressure displacement and magnetic separation for iron when lines of the same group and of the same type of separation are considered. In the case of titanium, for which it has not been possible to distinguish well-marked groups of lines, no evidence of a connection with magnetic separation is found.

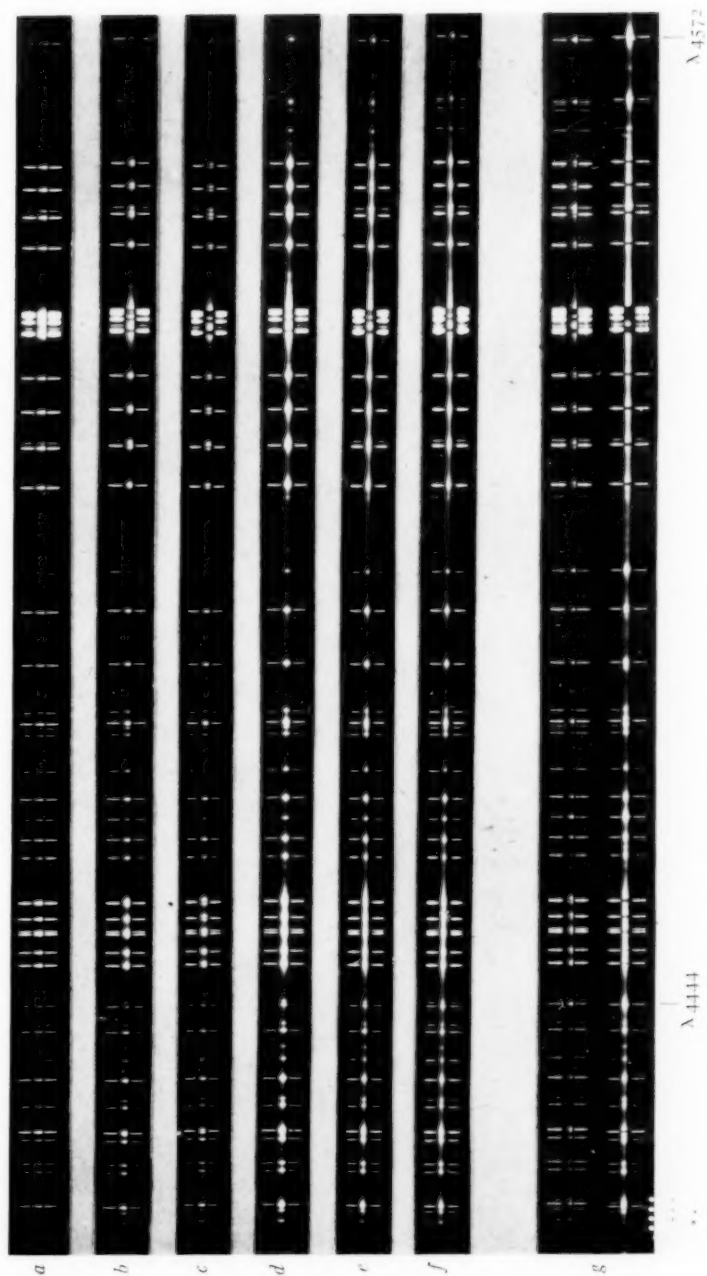
6. The values of the average displacement for the four iron groups at different wave-lengths are well represented by a law of variation of displacement with the third power of the wave-length. If we form simple means of the displacements of the titanium lines for considerable portions of the spectrum the values are well represented by a law of variation with the second power of the wave-length. The difference from iron may be due to the intermixture of various groups in the titanium spectrum. Measures of some calcium lines belonging to the second subordinate series indicate a variation of displacement according to the first power of the wave-length. The measures, however, are of low weight.

PLATE I



Mr. U

PLATE II



Ti are at different pressures; comparison at 1 atmosphere
a, b, c, d, e, f, at 2, 4, 6, 8, 12, and 16 atmospheres, respectively, above atmospheric pressure
g, h are in atmosphere of illuminating gas, at 4 atmospheres above atmospheric pressure

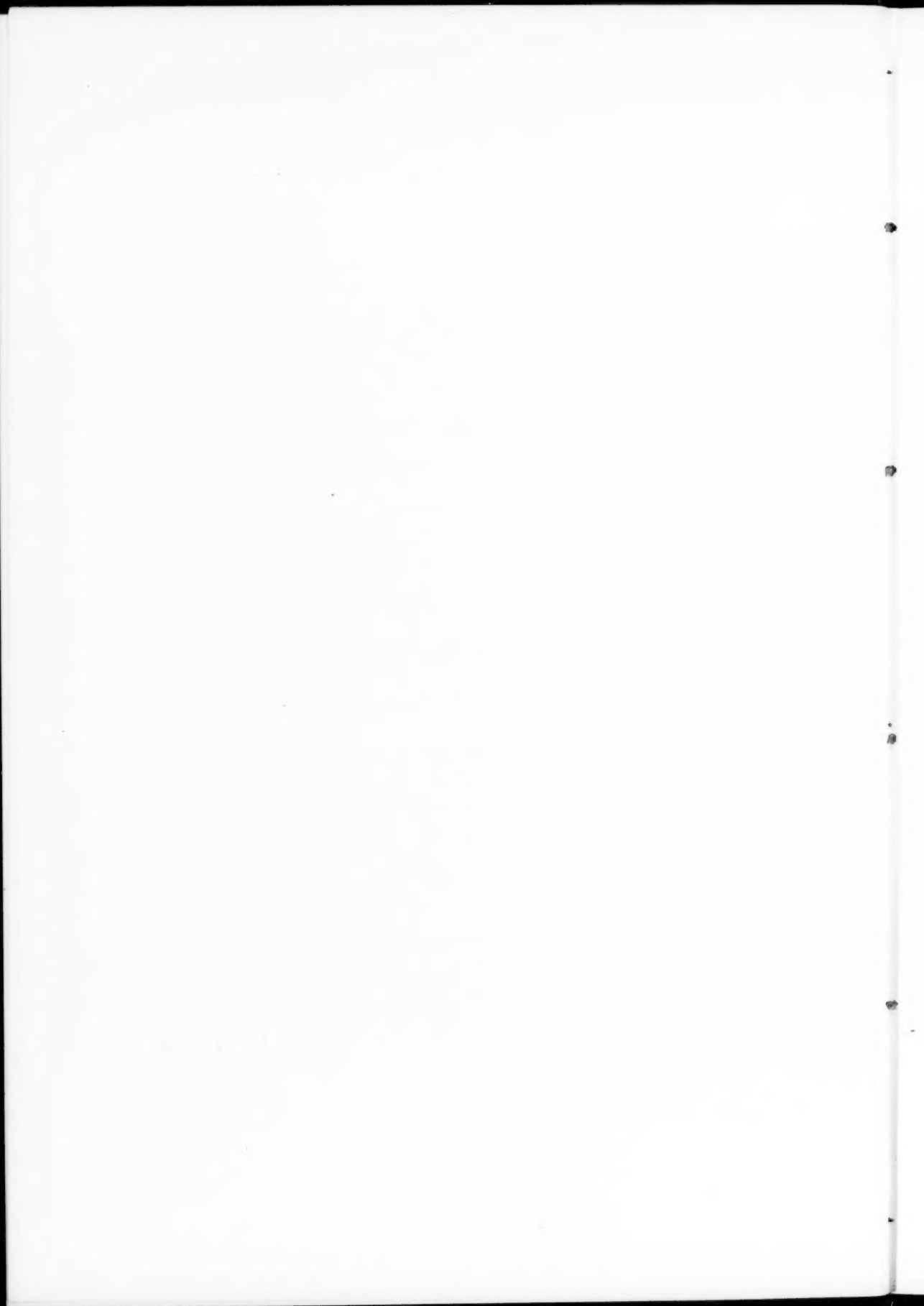
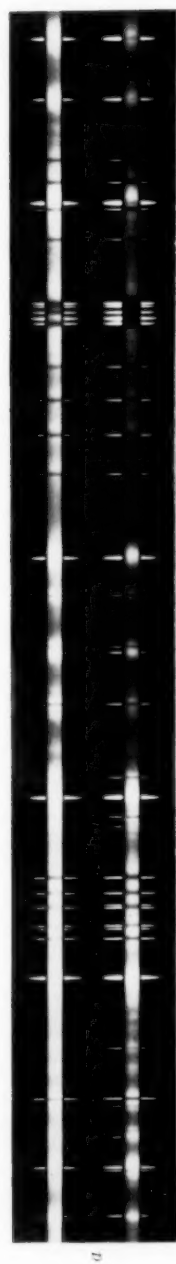
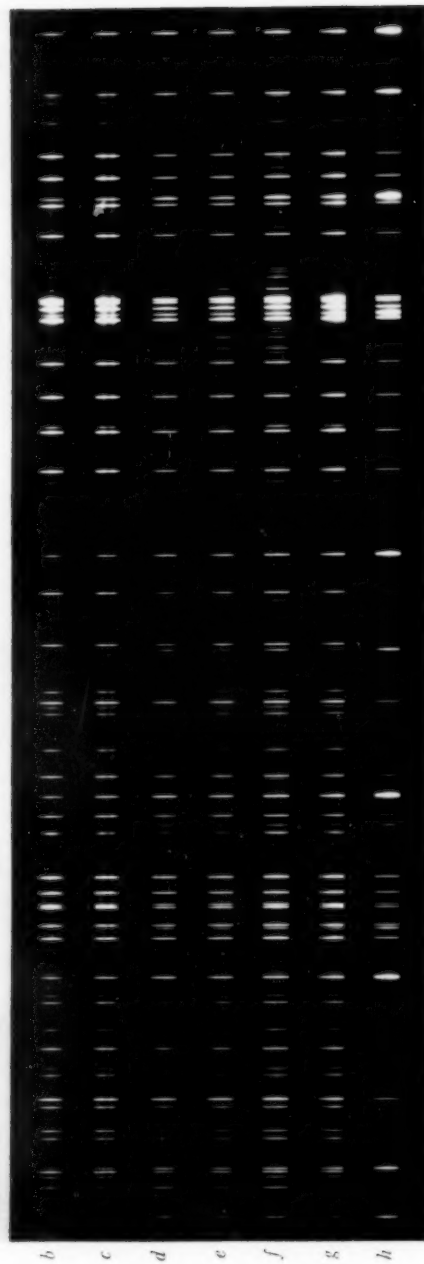


PLATE III



a



b

c

d

e

f

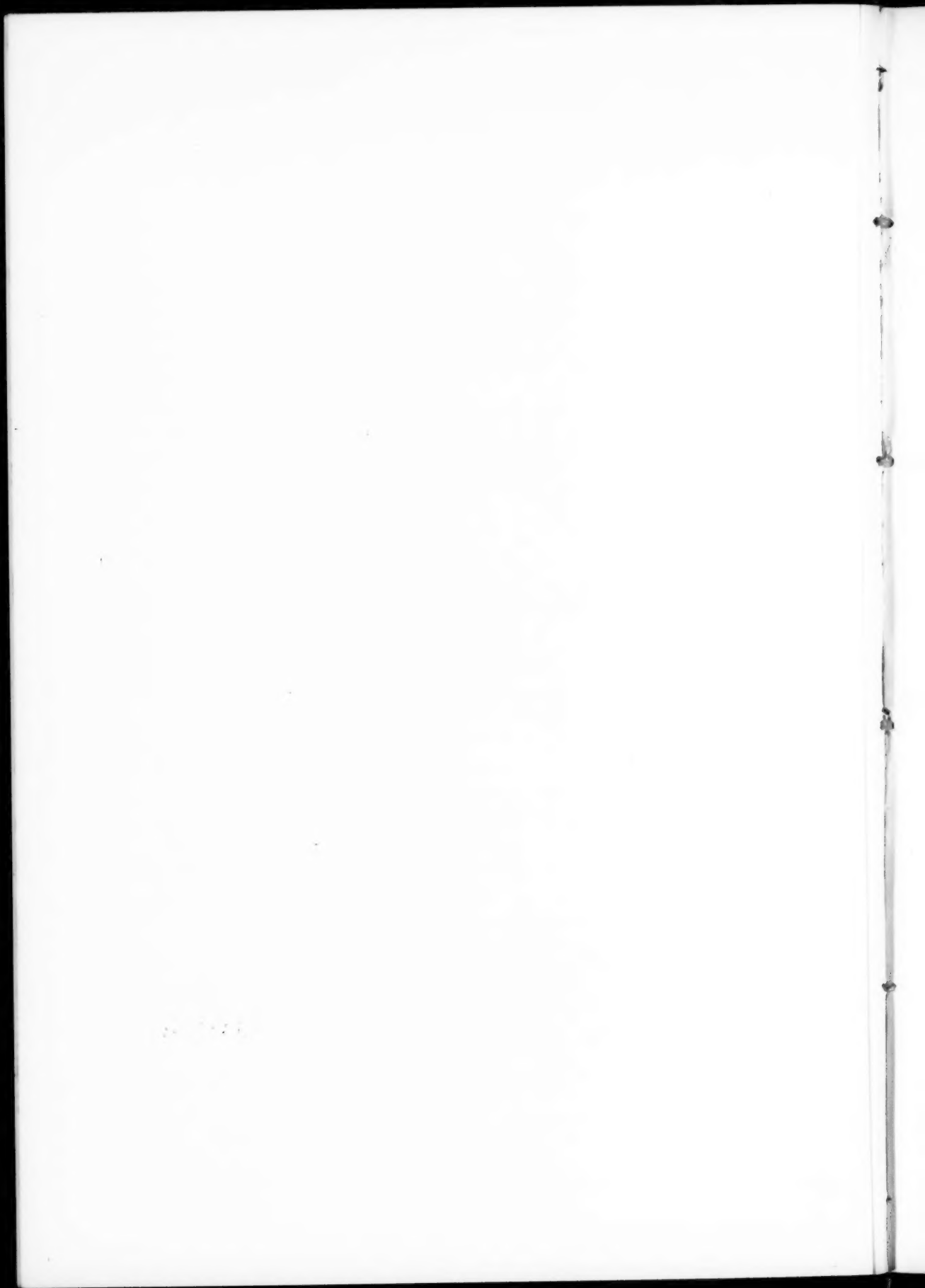
g

h

$\lambda 4444$

$\lambda 4572$

- a*, Ti spark, 0 atmosphere; comparison, spark at 1 atmosphere
- b* and *c*, arc 1 atmosphere
- d* and *e*, arc 10 cm
- f*, arc 1.5 cm
- g*, spark with self-induction and capacity
- h*, spark with capacity, but no self-induction



7. The displacements of the titanium arc lines are found to be accurately proportional to pressure for a range of from 2 to 16 atmospheres above atmospheric pressure.

8. The enhanced lines as a rule show much larger displacements under pressure than do the other lines in the titanium arc spectrum and are almost always unreversed. The amount of displacement, however, depends upon each individual line and a few enhanced lines give very small values.

9. In an atmosphere of hydrogen (illuminating gas) the displacements of the enhanced lines are appreciably larger than in an atmosphere of air or carbon dioxide at the same pressure. The other lines show the same displacements.

10. The displacements of the lines in the titanium spark appear to be larger on the average than in the arc, the largest differences being for the enhanced lines.

In the difficult work involved in the measurement of the photographs we have so far as possible followed the plan of having each plate measured by two observers. We are greatly indebted to Miss Lasby for her skilful treatment of the photographs and her active interest throughout the progress of the entire investigation.

MOUNT WILSON SOLAR OBSERVATORY
November 1911

THE SELECTIVE REFLECTION OF SALTS OF CHROMIUM AND CERTAIN OTHER OXYGEN ACIDS¹

BY HERBERT A. CLARK

As long ago as 1868, Mendeléjeff and Lothar Mayer announced the periodic system of the elements, according to which the physical and chemical properties of the elements are, apparently, periodic functions of their respective atomic weights. Two years earlier, R. Bunsen² found that solutions of different salts of didymium show absorption bands which are shifted toward the red end of the spectrum with increase in the molecular weight of the salt.

From then until now, a bewildering mass of data has been obtained by W. N. Hartley, E. C. C. Baly, H. C. Jones, W. W. Coblentz, H. Ley, and others, to get at the relations between the absorption spectra of solutions, principally in the visible and photographic regions, and their chemical constitution. Hartley,³ using solutions of simple metallic nitrates; H. C. Jones and J. A. Anderson,⁴ using solutions of the bromide and of the nitrate of cobalt; and E. C. C. Baly and C. H. Desch,⁵ comparing solutions of simple metallic nitrates with the corresponding nitrites; all found the same kind of shift of absorption bands that Bunsen had found for didymium salts. The (emission) spectral series equations of Kayser and Runge for elements belonging to the same Mendeléjeff group, indicate the same sort of shift.

Much of the experimental evidence, however, is either negative or contradictory. Since nearly all of the absorption data are for solutions, many of these being of organic compounds, this is not to be wondered at—especially in view of the enormous complications introduced by variations in temperature, concentration, nature of the solvent, thickness of the absorbing layer of the solution, state of ionization, and in what the chemist tries to account for

¹ *Phoenix Physical Laboratory Contributions*, No. 25.

² *Poggendorff's Annalen*, **128**, 100, 1866.

³ *Jour. Chem. Soc.*, **81**, 571, 1902.

⁴ "Absorption Spectra of Solutions," *Carnegie Publication No. 110*, p. 30.

⁵ *Jour. Chem. Soc.*, **93**, 1757, 1908.

under the name of stereochemistry. Consequently it would seem that fundamental relations between molecular and atomic weights and optical properties might well be looked for first in the reflection spectra, which show only the presence of such absorption bands as are very intense, and hence are the more characteristic.

Drude¹ has shown that in substances with normal dispersion ultra-violet absorption bands are probably due to resonance of negative electrons, having the same value of e/m as have cathode rays; and the infra-red bands, to resonance of masses of the size of a positively charged atom or molecule. Consequently reflection bands in the infra-red spectrum are more likely to be characteristic of a substance than are the ultra-violet maxima. The enormous extent of the infra-red region relative to that of the shorter wave-lengths is also in favor of the former region, in a search for fundamental relations.

A. H. Pfund² concluded from his data on the infra-red reflection from certain simple inorganic salts that the mechanism giving rise to these maxima is localized in the acid radical. Soon after, W. W. Coblentz³ found that the infra-red reflection maxima of certain sulphates and carbonates are shifted toward the long waves with increasing atomic weight of the base. Next, L. B. Morse⁴ found that, in certain simple inorganic salts of oxygen acids having a common base, the infra-red reflection maxima are shifted toward the long waves, as the weight of the element in the acid radical which is combined with a *constant* amount of oxygen increases. If it is assumed that a strong reflection maximum is a resonance effect, that the oxygen atom in the molecule is the resonator, and that the resonator is closely loaded with other oxygen atoms and with the acid-forming element in the molecule, but is loosely loaded with the base, the above results are consistent with one another, as well as with the chemists' views regarding the strength of the different "bonds" in the molecule. The present work was undertaken to test the conclusions of Pfund, of Coblentz, and of Morse, by the infra-red reflection from the salts of the chromium acids.

¹ *Annalen der Physik* (4) **14**, 958, 1904.

² *Astrophysical Journal*, **24**, 40, 1906.

³ *Phys. Rev.*, **25**, 136, 1907.

⁴ *Astrophysical Journal*, **26**, 242, 1907.

APPARATUS

A common arrangement for infra-red work, a Nichols radiometer with a reflection spectrometer having a rock-salt prism and a Wadsworth¹ mirror, was used. The apparatus was, in the main, the same as was used by L. B. Morse² in his work on the carbonates, and hence will be described somewhat briefly.

The optical system.—An image of the source, a Nernst glower, *A*, Fig. 1, was cast by the silvered concave glass mirror, *B*, upon the (plane) surface under investigation at *D*, at an angle of incidence of about 6° . An image of this image, in turn, was cast upon

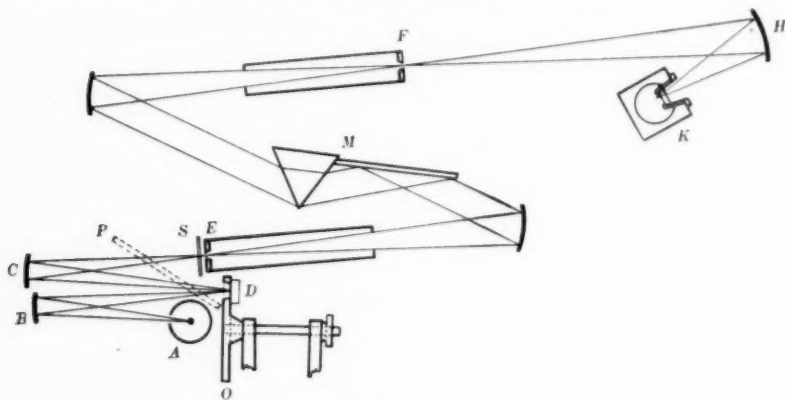


FIG. 1

the collimator slit, *E*, of the reflection spectrometer, by a second mirror, *C*. After resolution by the spectrometer, an image of the telescope slit, *F*, was cast by the mirror, *H*, upon one vane of the Nichols radiometer, *K*.

The spectrometer was a Schmidt and Haensch instrument with mirrors of 4 cm aperture and 35 cm focal length. The prism was of rock-salt, with faces 5 cm \times 8 cm and a refracting angle of $59^\circ 57' 20''$. The Wadsworth mirror-prism, *M*, enabled the spectrometer arms to remain fixed. The two slits, always of equal width, were as narrow as possible, consistent with sufficient energy. The usual range of slit-widths (varying from 0.30 to 1.00 mm for wavelengths longer than 9.0μ) is indicated in Fig. 4. No change of

¹ *Phil. Mag.* (5), **38**, 337, 1894.

² *Loc. cit.*

slit-width was ever made, however, while passing over a reflection maximum. The same figure also shows the slit-width at one point ($11.0\ \mu$) in terms of the wave-length interval entering the radiometer when the spectrometer is set for that particular wave-length, an interval of $0.16\ \mu$ at this point for slit-widths of $0.30\ \text{mm}$. This range increases to $0.21\ \mu$ for slit-widths of $0.50\ \text{mm}$ at a wave-length of $12.5\ \mu$; to $0.30\ \mu$ for slit-widths of $0.80\ \text{mm}$ at $14.0\ \mu$; and to $0.36\ \mu$ for slit-widths of $1.00\ \text{mm}$ at $15.0\ \mu$.

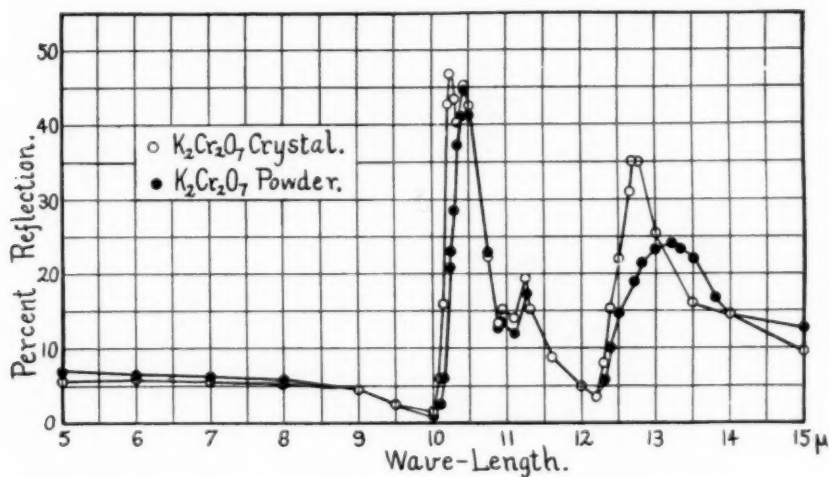


FIG. 2

Wave-lengths.—The deviations necessary to obtain representative wave-lengths were calculated in the usual way, from the indices of refraction for rock-salt as given by H. Rubens¹ and by H. Rubens and A. Trowbridge,² and a calibration-curve was plotted. The indices as given in the latter paper were corrected to agree with corrections found in a reprint. The calibration-curve was tested by means of the two sylvite absorption bands and the long wave-length reflection band of calcite. An air-tight metal-and-glass hood with engine-oil seal was always kept over the prism when it was not in use. A vessel of P_2O_5 was kept near the prism, under the hood, as a drying agent.

¹ *Annalen der Physik*, **54**, 482, 1895.

² *Ibid.*, **60**, 733, 1897.

Source.—A direct-current Nernst glower, consuming 132 watts at 110 volts, in series with a low-reading ammeter and a rheostat for close adjustment, was operated from a 70-cell storage battery. This arrangement enabled variations in the energy of the glower to be made inappreciable. The largest obtainable glower was used, in order that the greatest slit-width (1.0 mm) should be well covered by the image of the glower.

The *Nichols radiometer* had mica vanes, about 0.75 mm by 5.0 mm (a little larger than the image of the slit as cast upon the vane), placed about 5.0 mm apart, blackened with platinum black and shellac. The rock-salt window was protected by a P_2O_5 dryer when not in use. The period (time of swing of the vanes one way) varied from 40 to 60 seconds, according to the air-pressure, which was adjusted according to the speed or sensibility desired. The radiometer was wrapped in a thick layer of felt and covered with a box of heavy sheet copper, to protect it from sudden changes of room temperature. This proved so effective that the radiometer zero seldom drifted, due to varying room temperature, more than 1.0 cm during a half-day's "run." What drift there was, was very slow and steady. The reflection from silver, using a 1.0 mm slit, gave a scale reading of 54 mm at $15.0\ \mu$ and of 18 mm at $16.3\ \mu$; while the zero drift was so slight that an accumulation of observations would determine deflections of 3 mm to a few per cent. To indicate deflections (which could be estimated to 0.1 mm), the image of a fine wire in front of an 88-watt Nernst glower was projected on a millimeter scale (not shown in Fig. 1) at a meter's distance, by a small, platinum-plated, concave mirror¹ attached to the radiometer suspension. This glower, being in parallel with the source, was so steady that it did not affect the radiometer zero perceptibly, after the first large shift due to lighting the glowers. Numerous diaphragms were used, to protect all parts of the entire optical system from any stray light, except for a faint, diffuse glow.

PURITY OF THE SPECTRUM

A very serious source of error in infra-red spectrum work is the unavoidable impurity of the spectrum. The present work deals principally with wave-lengths from $10.0\ \mu$ to $16.0\ \mu$, for which the

¹ See A. H. Pfund, *Astrophysical Journal*, 24, 22, 1906.

energy of a Nernst glower is extremely small as compared with that at $2.0\ \mu$ to $4.0\ \mu$, for instance. Consequently the presence of a very small part of the energy of the shorter wave-lengths occurring as an impurity in the spectrum of the longer, would constitute a very large part of the total (apparent) energy of the latter. This can readily cause a very large error, not only in the intensity of a reflection maximum, as measured, but also in its position, shifting it toward the shorter waves. To reduce this effect, screens

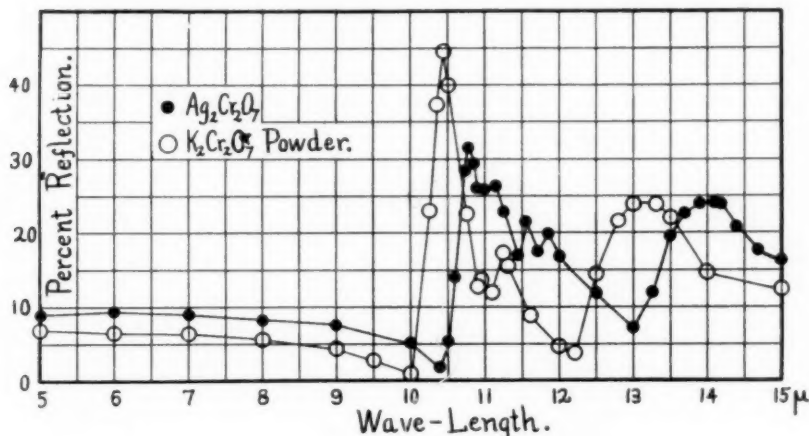


FIG. 3

were used (*S*, Fig. 1) which are opaque to the spectral region considered, but transparent for shorter wave-lengths.¹ They were arranged to slide smoothly in vertical ways in front of the collimator slit. A glass screen was used for wave-lengths from $5.5\ \mu$ to $10.0\ \mu$ or $10.5\ \mu$, according to the position of the reflection band; and one of fluorite for the longer wave-lengths (see Fig. 4). Even with this arrangement, however, there probably is enough stray energy at the longest wave-lengths to affect the results considerably. The blackened wood shutter, *P*, Fig. 1, was used for wave-lengths shorter than $5.5\ \mu$.

MOUNTING THE SPECIMENS

Each specimen (*D*, Fig. 1) was mounted on the rear of a wheel, *O*, to cover a hole in the wheel. A plane-glass mirror, silvered on

¹ See Rubens and Hollnagel, *Phil. Mag.* (6), **19**, 765, 1910.

the front face, was mounted in another hole 60° away. Reflection from this silver comparison mirror was assumed to be 100 per cent, probably a trifle too large.¹ This assumption introduces a very slight error in the height of the reflection curve, but not in its shape. The assumption is thus justifiable, especially in view of the fact

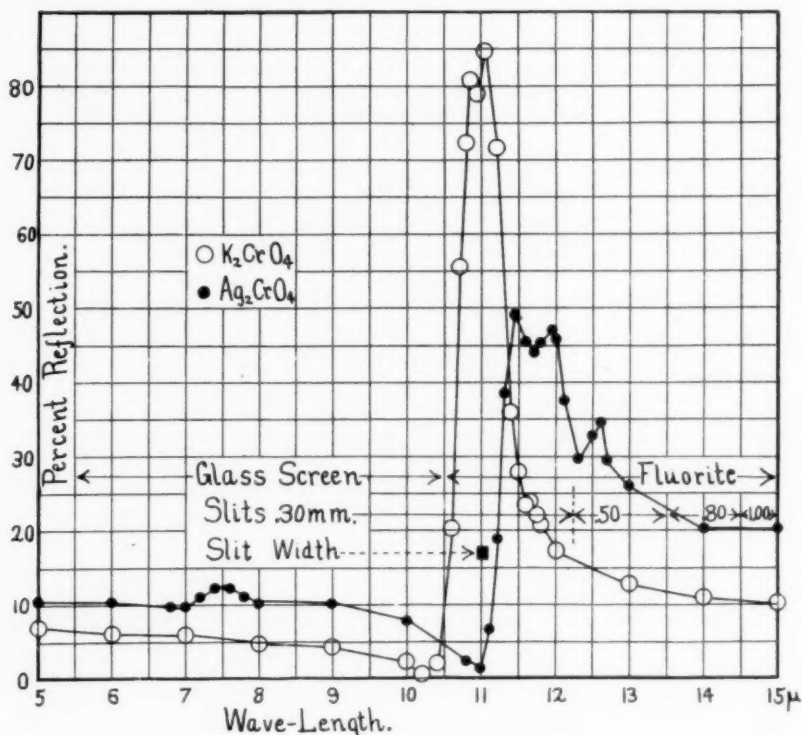


FIG. 4

that the polish of the different reflecting surfaces was unavoidably different. Rotation of the wheel between carefully adjusted stops served to place either surface, at will, in the optical path, in closely identical positions. The two surfaces were adjusted to the same plane by leveling screws, as determined by the reflection of an incandescent lamp filament from each surface, in turn, into a telescope having ocular cross-wires. This arrangement, which

¹ See Hagen and Rubens, *Annalen der Physik* (4), **11**, 873, 1903.

worked very smoothly, with neither jar nor lost motion, proved entirely satisfactory. Cords served conveniently to manipulate the wheel and the screens, from the viewer's seat at the reading scale.

SURFACES

Substances.—All of the salts of all the chromium acids available were ordered from the dealer. As many as possible were obtained from Kahlbaum; the rest were made to order, at considerable expense, by Theodor Schuchardt, of Görlitz. See the list in Table I. All were anhydrous as obtained from the makers, except the chromates of lithium, calcium, and magnesium. The second one of these was made anhydrous by heating in a drying oven; the others could not be entirely dried. This is mentioned again, under the discussion of the curves.

Preparation of the surfaces.—Many of the salts were obtainable only in the form of a fine powder; consequently, all were powdered, sifted through a very fine geologist's sieve, and compressed into cakes in a hydraulic press under about 30 tons per square inch (a method used previously by Miss Langford¹ for the phosphates, in the Phoenix Physical Laboratory), then polished, if possible, to give a plane reflecting surface. These are designated hereafter as "polished powder" surfaces. Some were too friable to be polished at all, so they were pressed against a piece of plate glass under about 12 tons per square inch. The removal of the glass left a reflecting surface that was more or less brilliant in every case but one, $BaCr_2O_4$. The obtainable polish varied greatly with the substance. A number of the surfaces reflected poorly in the visible region. The image of an Edison lamp filament at nearly perpendicular incidence, however, could be seen when adjusting, in all except two, $CaCrO_4$ and $BaCr_2O_4$. It was necessary to use a Nernst glower at perpendicular incidence in adjusting the former, and at an angle of incidence of about 45° for the latter. The lack of a perfect polish, however, affects the magnitude, but not the position, of a resonance maximum. These surfaces are hereafter designated as "glass" surfaces. One salt, $CaCr_2O_4$, resisted both these methods; hence a thin plate of rock-salt was pressed lightly

¹ *Physical Review*, 33, 138, 1911.

against the powdered chromite contained in a cavity in a piece of cork, and the reflection was measured from the chromite-rock-salt surface. Such surfaces are hereafter designated as "rock-salt" surfaces. Two other salts (Li_2CrO_4 and MgCrO_4) are so very deliquescent that sufficiently permanent surfaces could be prepared only in this way. The nature of each surface is indicated in Table I. All curves are for "air" surfaces (either "polished powder" or "glass" surfaces) except as otherwise designated on the curves. Surfaces of several of the less troublesome salts, already prepared

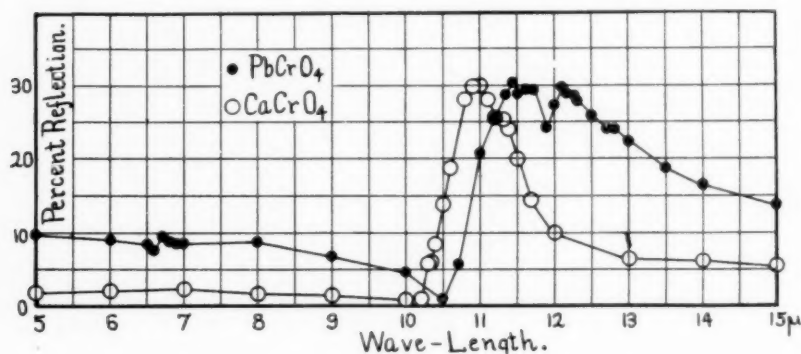


FIG. 5

in one of the first two ways and measured, were made by the third method also, to serve as a check on this method. (See Table I.)

The selective absorption of rock-salt in the long wave-length region of the spectrum would have a tendency to shift the apparent location of resonance regions toward the shorter wave-lengths, when measurements are made on a "rock-salt" surface. An attempt to avoid this difficulty was made by placing a similar plate of rock-salt over the silver comparison mirror. To do this, two large, slightly prismatic plates of rock-salt were polished on both sides; these each had a mean thickness of 2.60 (± 0.005) mm and a refracting angle of 53' ($\pm 5'$). Each large plate was then sawed up into smaller ones of the requisite size. The small plates were paired, one of a pair being chosen from each large plate to give two of the same thickness. One of a pair was then put on a powder surface, as mentioned before, and the other was put about

TABLE I

TYPICAL FORMULA	SALT	SURFACE	WEIGHT OF BASE IN MOLECULE	WEIGHT IN ACID RADICAL WITH O ₃	Probably Impurities	REFLECTION MAXIMA			
$M'Cr_2O_7$	$Ag_2Cr_2O_7$	"polished powder"	215.8	44.6	10.78	11.15	11.54	11.88
	"	"rock-salt"	"	"	"	"	"	14.05
	$K_2Cr_2O_7$	"crystal"	78.2	"	10.25	10.45	10.96	11.23
	"	"polished powder"	"	"	"	10.45	10.96	11.23
M'_2CrO_4	"	"rock-salt"	"	"	"	10.4	"	13.15
	Ag_2CrO_4	"polished powder"	215.8	39.0	7.5	11.45	11.95	12.60	12.6
	K_2CrO_4	"	78.2	"	10.86	11.05	11.65	"
	* Li_2CrO_4	"rock-salt"	14.0	"	"	10.75	"	"
$M''CrO_4$	$PbCrO_4$	"glass"	207.1	"	6.7	11.45	11.65	12.10	12.80(?)
	$BaCrO_4$	"	137.4	"	10.90	11.08	11.58	12.60
	$SrCrO_4$	"polished powder"	87.6	"	10.48(?)	10.65	11.35	11.80
	† $MgCrO_4$	"glass"	40.1	"	12.1	"	10.32(?)	10.96	11.30
$M'''CrO_4$	* $MgCrO_4$	"rock-salt"	24.3	"	"	"	10.90	"
	$BaCr_2O_4$	"glass"	137.4	78.0	11.5	15.0	15.95	"	"
	$CaCr_2O_4$	"rock-salt"	40.1	"	14.6	15.4	"	"
	(observed)	"	"	"	15.2	16.0	"	"
$M''''CrO_4$	$CaCr_2O_4$	(calculated for air)	"	"	"	"	"	"
	(corrected)	"glass"	24.3	"	15.0	15.8	"	"
	$MgCr_2O_4$	"rock-salt"	"	"	14.4	15.2	"	"
	"	"	"	"	"	"	"	"

* Not anhydrous.

† Made anhydrous by heating.

1.0 cm in front of the silver comparison mirror, far enough away to avoid interference due to multiple reflection. The energy reflected from the *front* surface of each of the rock-salt plates was sent out of the optical system, due to the angle between the two surfaces. That reflected from the *rear* surface of that plate which was over the silver comparison mirror, was sent off similarly, since the whole plate was tilted slightly with respect to the mirror. Calculation shows that the beam is shifted at the collimator slit, by the thin prism, a distance of 0.6 mm more for a wave-length of $15\ \mu$ than for the sodium line, for which the mirrors *B* and *C*, Fig. 1,

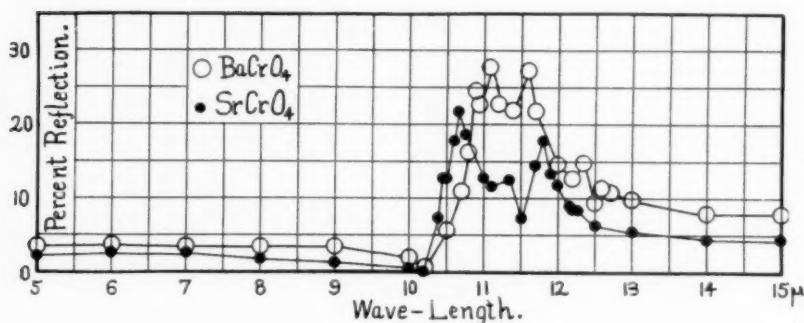


FIG. 6

were adjusted. Unfortunately, this was not determined until it was too late to repeat the observations. The refracting edges of both prisms of a pair, however, were turned the same way; thus the shift of the beam would diminish the *absolute* amount of energy entering the spectrometer, but not the *relative* (i.e., the percentage reflection). Further, if the reflection maxima are due to true resonance, it ought not to be necessary to focus the "reflected" beam exactly on the spectrometer slit.¹ It would seem, therefore, that the only effect of the rock-salt plate upon the reflection maxima would be due to the fact that the reflection takes place from a chromate-rock-salt, instead of from a chromate-air surface. This would merely reduce the amount of the reflected energy, due to the smaller variation in refractive index at the reflecting surface; but should not, supposedly, alter the *position* of the maximum,

¹ See J. A. Anderson, *Astrophysical Journal*, **26**, 73, 1907.

since the refractive index of rock-salt has not yet begun to change very rapidly. Why this method does not eliminate all shift in the positions of the maxima, is not at present clear. That it does not do so is evident from the shift in the $13\ \mu$ and the $15\ \mu$ bands, Fig. 10. This will be considered further in the discussion of the results from "rock-salt" surfaces.

Permanence of surfaces.—Measurements on the surfaces were taken over a period of from one day to three months each, varying with the surface. In no case was any variation in the reflecting surface detected, either visually or by means of the measurements, except in the cases of $BaCrO_4$, of $PbCrO_4$, and of $Ag_2Cr_2O_7$ when under rock-salt. The first showed a slight darkening over the entire surface exposed to the air, after a period of three months. An unavoidable interruption in the work scattered observations on this surface over that length of time. The observations indicated no change in the surface during that period. The $PbCrO_4$, after three weeks, showed a streak, slightly darker than the background, over the small part of the surface which was covered by the image of the Nernst glower (the source). Again the data gave no evidence of any change in the surface. The $Ag_2Cr_2O_7$ when put under rock-salt, changed immediately to $AgCl$, judging from the immediate change in color of the powdered salt. This is mentioned later, in the discussion of the results from the "rock-salt" surfaces.

METHOD OF OBSERVING

A zero reading was taken before and after each deflection, to detect any zero drift. Two or more readings were taken for each wave-length from the surface under investigation, then from the silver comparison surface, before disturbing the wave-length setting. Many of the observation points are omitted from the published curves where the trend of the curve is regular, to avoid crowding the points. The observation points were usually $0.5\ \mu$ apart for the flat, short wave-length portion, and $0.1\ \mu$ to $0.2\ \mu$ apart for the longer wave-lengths, except when going over the sharp reflection peaks from $10\ \mu$ to $12\ \mu$. Here they were from $0.02\ \mu$ to $0.05\ \mu$ apart. At least two observations were taken at every point. When these differed appreciably, they were repeated

until a consistent series was obtained. Observations began, in every case, at the wave-length 1.5μ , except for a few of the "rock-salt" surfaces. However, since there was nothing of interest in the early infra-red, the curves are all plotted to begin at longer wave-lengths.

THE REFLECTION CURVES

"Air" surfaces.—Fig. 2 shows the results from a "polished powder" surface of $K_2Cr_2O_7$ and from the surface of an excellent crystal of the same, polished parallel to one of the cleavage planes.

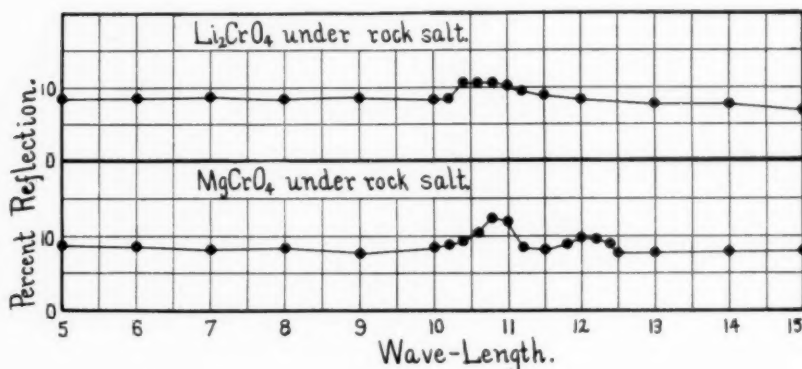


FIG. 7

This is the only crystal measured. The absence of the first (short-wave) peak from the "polished powder" surface, and the shifting of the last, will probably require polarized energy to explain.¹ J. T. Porter² had located a maximum for a polished crystal of $K_2Cr_2O_7$ at 10.3μ by the method of *Reststrahlen*. The "polished powder" curve is repeated in Fig. 3, for comparison with that of $Ag_2Cr_2O_7$, also a "polished powder" surface. The chromates of silver and potassium are shown in Fig. 4. (The nature of each surface is indicated in Table I.) Each has a single complex maximum, with three peaks. One peak in the latter, that at 11.65μ , is faint, but its presence is not in doubt. The potassium chromate curve is notable for its great intensity and sharpness; consequently

¹ See R. E. Nyswander, *Physical Review*, **28**, 291, 1909.

² *Astrophysical Journal*, **22**, 229, 1905.

it ought to prove a good source of *Reststrahlen*. The faint maximum in Ag_2CrO_4 at 7.5μ is assumed to be due to a trace of an impurity, possibly $AgNO_3$ (from which the chromate was probably made), which has a sharp maximum at 7.45μ . Arc spectrum photographs taken with a ten-foot concave Rowland grating, of each salt having a suspected impurity, did not, in any case, identify the impurity.

Fig. 5 shows the results from the chromates of lead and calcium. The calcium salt in the stock bottle was not anhydrous, but was made so by heating in an air-bath at $150^\circ C$. for eight hours. Since

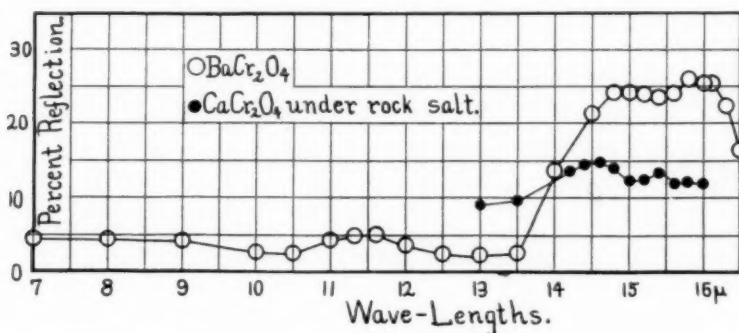


FIG. 8

no change could be detected in the surface after standing in the dry research-room during the period of observation, two days, it is assumed that it remained anhydrous. Each curve has a single complex maximum. The lead curve seems to have five peaks, two being so faint as to be somewhat in doubt (indicated by ? in Table I). The calcium curve has three maxima, one being somewhat in doubt. $PbCrO_4$ (Fig 5), like Ag_2CrO_4 (Fig. 4), has a low, short wave-length maximum, possibly due also to some unknown impurity. This chromate was probably made from the acetate; but the reflection curve of the acetate is unknown. L. B. Morse² had already roughly located a maximum in crocoite (natural crystal of $PbCrO_4$) at 11.5μ . For the chromates of barium and strontium,

¹ A. H. Pfund, *Ibid.*, 24, 35, 1906.

² *Physical Review*, 26, 525, 1908; see also W. W. Coblentz, "Investigations of Infra-Red Spectra," *Carnegie Publication No. 97*, p. 181.

see Fig. 6. Each has a single complex maximum with five peaks, two in the latter being somewhat in doubt. (See Table I.)

Magnesium chromite is shown in Fig. 9, and the chromites of barium and calcium in Fig. 8. The low maximum at 11.5μ in $BaCr_2O_4$ was suspected to be due to a trace of $BaCrO_4$ as an impurity (compare Fig. 6). A letter of inquiry to the maker, Theodor Schuchardt, confirmed this suspicion. The rapidly increasing absorption of the rock-salt prism and radiometer window, as well as the decreasing intensity of the source, with increasing wave-lengths, made observations to 16.0μ or 16.5μ (on the chromites)

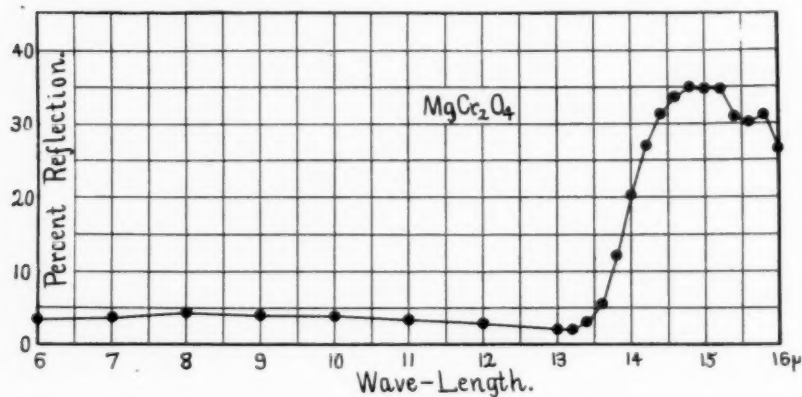


FIG. 9

extremely difficult. Probably the spectrum is decidedly impure here also, although a fluorite screen was used. Repeated observations were made to locate the maxima as definitely as possible. The order of accuracy has been indicated previously, under the discussion of the radiometer.

"Rock-salt" surfaces.—The chromates of lithium and magnesium are shown in Fig. 7. Both of these, as obtained from the stock bottle, contained water of crystallization. Attempts to dry them in an air-bath at $110^\circ C$. for twenty-four hours, still left about one molecule of water in the former, and two in the latter, as determined by analyses kindly made by Mr. R. F. McCracken, of the chemistry department at Columbia University. They were then so extremely hygroscopic, absorbing moisture readily even in the

artificially dried atmosphere of the research-room (kept below 60 per cent humidity), that they were mounted under rock-salt, as mentioned before, in holes lined with sealing wax, and hermetically sealed in.

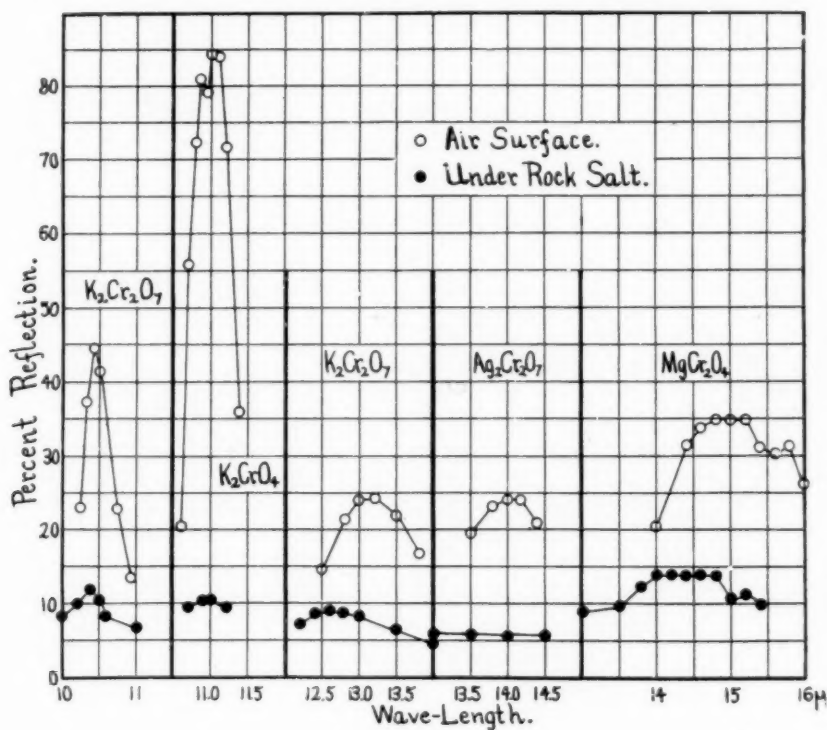


FIG. 10

The positions of the maxima in $CaCr_2O_4$ ("rock-salt" surface, Fig. 8) suggested a shift due to rock-salt, although an attempt has been made to eliminate the effect of the rock-salt, as has been described under the heading *Preparation of the surfaces*. To test this, measurements were made on a "rock-salt" surface of $MgCr_2O_4$ and compared with the "glass" surface curve (Fig. 9) of the same substance, which was in contact with the air. (See Fig. 10.) The shift toward the short waves (0.6μ for each peak), from the "air" surface to the "rock-salt" surface, is more evident

than is the cause. It is probably caused, however, by the selective absorption of rock-salt in this region of the spectrum. An attempt to determine this shift as a function of the wave-length resulted in the other curves in Fig. 10. At 10.5μ ($K_2Cr_2O_7$) and at 11.0μ (K_2CrO_4), there is no observable shift. At 13.0μ ($K_2Cr_2O_7$), the shift is practically the same as at 15.0μ ($MgCr_2O_4$). The shift

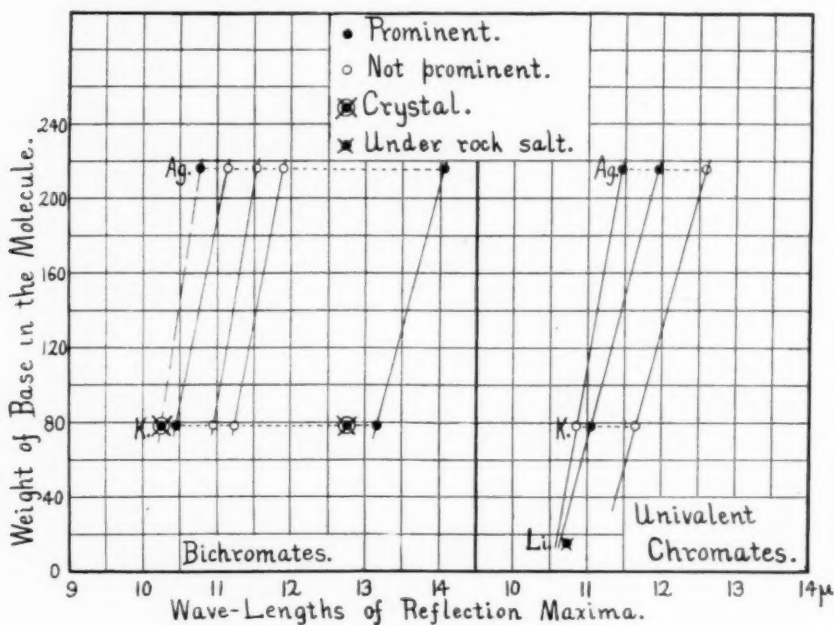


FIG. 11

at 14.0μ could not be determined. The $Ag_2Cr_2O_7$ changed color immediately on contact with the rock-salt surface, probably due to formation of $AgCl$. The absence of a reflection peak confirms this view. These are the only surfaces whose maxima seemed sharp and prominent enough for such a test. These data are not sufficient to locate the curve desired, especially as the exact location of the centers of such broad, low maxima is very much in doubt. However, all the maxima located under rock-salt except one (the 12.1μ band in $MgCrO_4$) are in one of two regions; between 10.5μ and 11.0μ where the shift is zero, and near 15.0μ where

the shift is 0.6μ . These shifts are assumed to be characteristic of their respective wave-lengths, only. Consequently Table I shows both "observed" and "corrected" locations of the resonance maxima for the only substance concerned, CaCr_2O_4 , the corrected wave-length being calculated by assuming that the shift for this surface is the same as for MgCr_2O_4 under rock-salt (Fig. 10). It seems likely that the 12.1μ band in MgCrO_4 (Fig. 7) may be shifted a little toward the short waves, as are bands in other substances at 13μ and at 15μ (Fig. 10) by the rock-salt cover plate.

SHIFT OF MAXIMA WITH WEIGHT OF BASE

Attempts to plot the shift of position of reflection maxima, with atomic weight of base or with total weight of base in the molecule, proved fruitless until the salts considered were limited, in any one comparison, to those having a single typical formula. This, probably, is to be expected. Consequently the bichromates, the univalent chromates, the bivalent chromates, and the chromites are tabulated and plotted separately in Table I and in Figs. 11 and 12. In the typical formulae, M' represents any univalent base; and M'' , any bivalent base. Shift lines are drawn for each separate peak in the complex maxima, since many of the maxima are so broad and complicated that their centers of gravity are indeterminable. To compare these results with those of other observers, corresponding data for sulphates, nitrates, silicates, and carbon-

TABLE II

Typical Formula	Salt	Weight of Base in Molecule	Reflection Maxima			Authority
$M''\text{SO}_4$	BaSO_4	137.4	8.35	8.9	9.1	Coblentz
	SrSO_4	87.6	8.2	8.76	9.1	"
	CaSO_4	40.1	8.6	9.1	"
$M'\text{NO}_3$	AgNO_3	107.0	7.45	Pfund
	KNO_3	39.1	7.05-7.15	Pfund and Coblentz
$M''\text{SiO}_3$	CaSiO_3	40.1	9.2	Morse
	MgSiO_3	24.3	9.1	Coblentz
$M'''\text{CO}_3$	PbCO_3	207.1	7.2	11.94	14.8	Morse
	BaCO_3	137.4	6.86	11.60	14.5	"
	SrCO_3	87.6	6.76	11.56	14.37	"
	CaCO_3	40.1	6.6	11.31	14.2	"

ates are plotted in Fig. 13. (See Table II.) These include all the data obtainable for salts of simple inorganic acids, except those containing water of crystallization, and those which are the sole representatives of their own typical formulae. For the sake of brevity, merely a part of the data on one, only, of the carbonate bands, is given; the abbreviation does not affect the following conclusions.

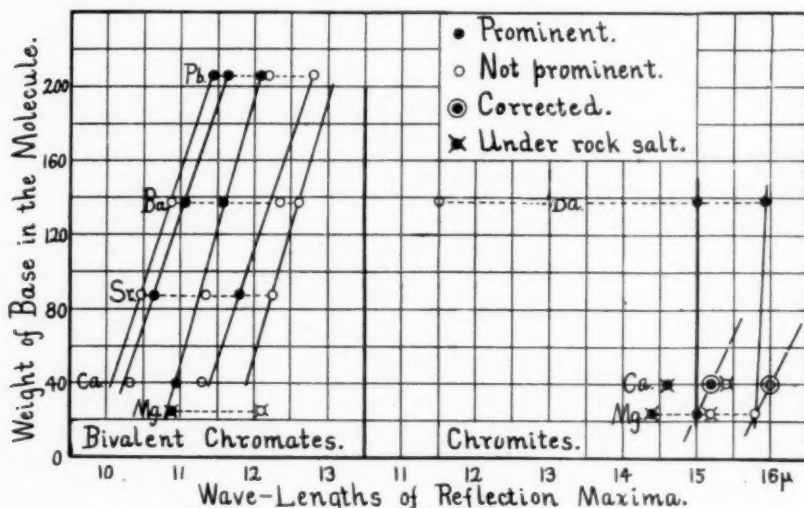


FIG. 12

The chromite shift (Fig. 12) seems so erratic that it will not be considered further in this connection. This may be due, at least in part, to the difficulty with which measurements are made in this region; also to the fact that the maxima are not very definitely located, being broad and low, as well as to the effect of the rock-salt cover plate; all of these chances for error are discussed above. The stray maximum at 11.5μ in $BaCr_2O_4$ is due to $BaCrO_4$, as mentioned before. W. W. Coblentz¹ gives the reflection of iron chromite from 1.0μ to 11.0μ , practically constant at 4 per cent. This result is consistent with the present work on the chromites of barium, calcium, and magnesium.

It is unfortunate that many of the shifts are determined by

¹"Investigations of Infra-Red Spectra," Carnegie Publication No. 97, p. 15.

only two points, especially when those points are as close together as in the case of the silicates (Fig. 13). They are given merely for what they are worth, only for the sake of completeness, without attaching much value to the silicate shift lines; or, possibly, even to the nitrate. The Li_2CrO_4 (Fig. 11) point is so low and faint that it may conceivably belong exactly on the second shift line. Similarly, the 10.9μ band in MgCrO_4 (Fig. 12) may readily belong on the third shift line. The shift lines suggest that the 12.1μ

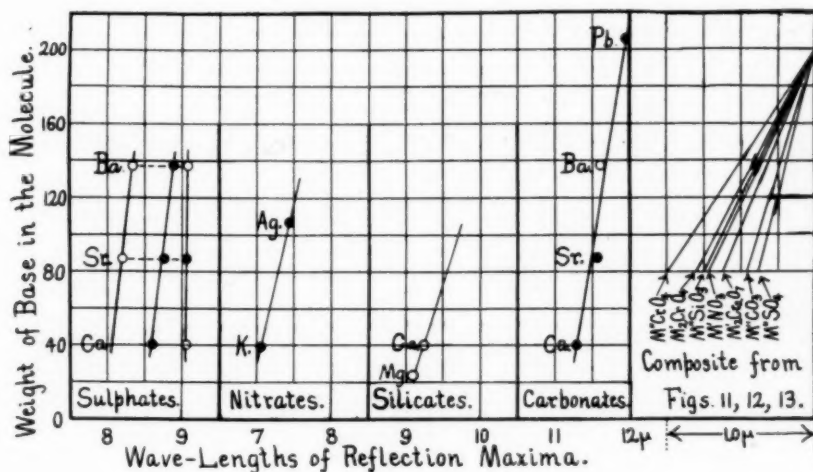


FIG. 13

band in this last salt is due to an impurity. It is possible also that it really belongs at a longer wave-length, as was suggested above. This salt contains about two molecules of water. Rubens and Ladenburg's¹ work on the reflection from water does not suggest the presence of anything in this region of the spectrum due to water. However, their work was on pure water, not on a salt whose molecules may be loaded down with water. Li_2CrO_4 (Fig. 7) also contains water (about one molecule), but its curve gives no indication of it. It is conceivable that a sufficiently high resolving power and amount of energy would show that CaCrO_4 and MgCrO_4 (Figs. 5, 7, and 12) have five peaks, like their neighbors; and,

¹ *Verhandlungen der Deutschen Physikalischen Gesellschaft*, 11, 16, 1909.

correspondingly, Li_2CrO_4 (Figs. 7 and 11), three peaks. The bivalent sulphates¹ show a similar simplification of a complex band as the atomic weight of the base is decreased.

One shift line from each of these types of salts (except the chromite) is collected in the "composite" in Fig. 13, all plotted from a common point, to show the relative rate of shift. The second (from the short wave-length side) shift line is chosen, some-

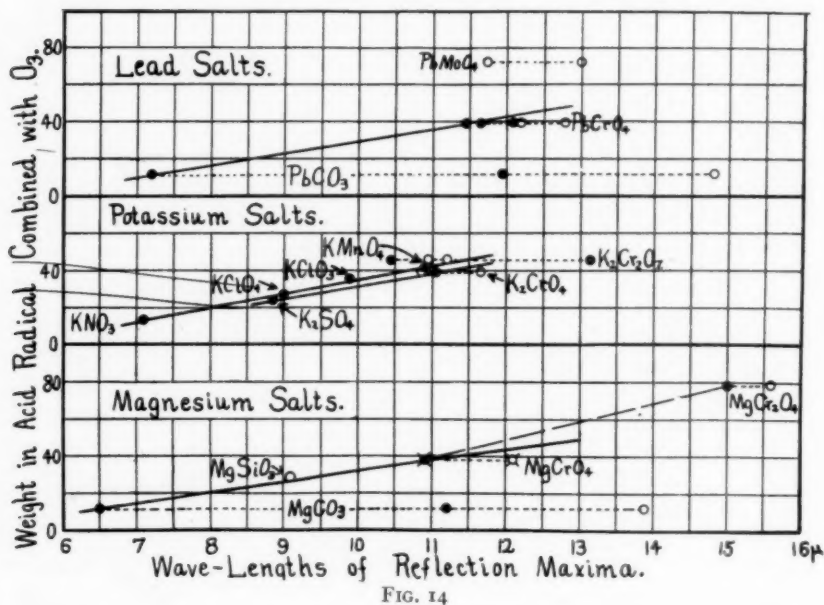


FIG. 14

what arbitrarily, from the bichromates, the univalent chromates, and the sulphates; and the third, from the bivalent chromates. The "composite" has the same scale of ordinates as the others but the scale of abscissas is doubled, to separate the lines somewhat more. The chance for error in determining the exact direction of some of these lines, as mentioned above, is so great that little or no dependence can be placed on their exact order. There seems to be no question, however, that the rate of shift varies with the type of salt.

¹ W. W. Coblentz, "Investigations of Infra-Red Spectra," *Carnegie Publication No. 65*, pp. 77-79.

SHIFT OF MAXIMA WITH WEIGHT IN ACID RADICAL

Figs. 14, 15, and 16 show the positions of resonance maxima as plotted against that fractional part of the total weight of the characteristic element in the acid radical, which is combined with an arbitrarily fixed amount of oxygen, O_3 .¹ For instance, in any carbonate, as $MgCO_3$, the atomic weight of carbon, 12, is the plotting value; but in a sulphate, as $MgSO_4$, three-fourths of the atomic weight of sulphur ($\frac{3}{4} \times 32 = 24$), which is the amount of sulphur combined with three parts of oxygen, O_3 , is the plotting value; similarly for the salts of other acids. In order that the observed shift may be due to the acid radical alone, salts of any one base, only, are compared with one another. The data for these curves (see Table III) as for Figs. 11 to 13, inclusive, contain all the data obtainable from all observers, for salts of simple inorganic acids, except those containing water of crystallization, and those individual salts which have the exclusive use of their respective bases. The uncertainty as to the exact direction of these shift lines is even greater than in Figs. 11 to 12, since the different salts of any one base do not always have the same number of peaks, nor are their peaks arranged in the same order of intensity. Here, again, some of the shift lines are, unfortunately, defined by two points, only; this is particularly undesirable in the case of the silver salts, for which the points are very close together. The attempt was made to locate the shift lines by the points which are the most prominent, and hence, presumably, the most nearly representative.

In Fig. 14, $PbMoO_4$ seems entirely out of harmony with the other lead salts. The potassium salts show two shift lines; one for the univalent acids and one for the bivalent. It is hardly to be expected that the two should coincide. The lone dichromate is out of harmony with both of these shift lines. However, it seems just a little surprising that salts in which *both* parts of the acid radical change (as KNO_3 and $KClO_4$) should line up together as well as they do. On the other hand, the relation between these two salts seems much simpler than that between $K_2Cr_2O_7$ and any of the other potassium salts, unless we assume the impossible hypothesis that all the atoms of one kind in a molecule are rigidly locked

¹ L. B. Morse, *Astrophysical Journal*, **26**, 241, 1907.

together. These curves would suggest, therefore, what is not inconceivable, that the shift lines of the O_3 and the O_4 acids are so close together as to be indistinguishable, while that of the O_7 acids is observably different from each of the others.

The magnesium salts (Fig. 14) show another variation, the line connecting $MgCrO_4$ and $MgCr_2O_4$ (broken line) having less slant than the main (solid) shift line. However, it would be rather surprising if this were not the case. It is hardly conceivable that *two*

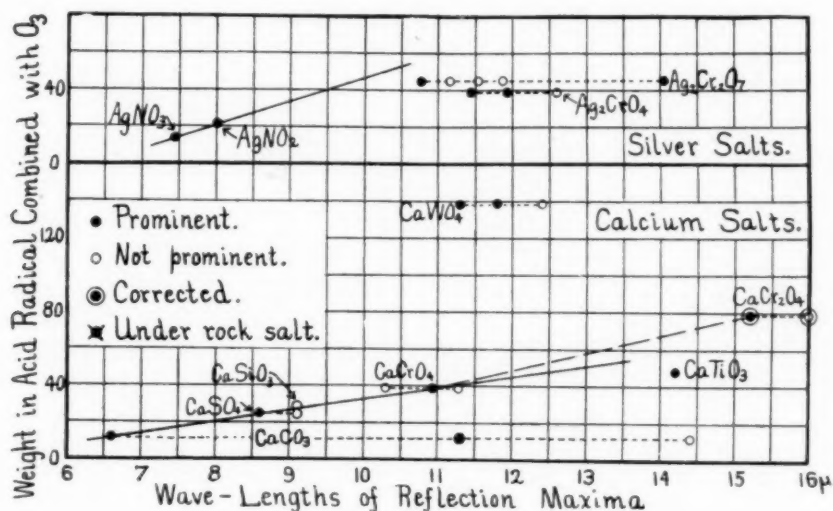


FIG. 15

atoms of chromium would have the same effect upon the shift as a single atom having *twice* the atomic weight of chromium. Fig. 12 suggests that the 12.1μ band in $MgCrO_4$ is due to an impurity; Fig. 14 suggests the same. The short wave-length peak is chosen, somewhat arbitrarily, in all the chromites, in locating the shift line. Choosing the other point would, however, affect the above conclusions in degree only, not in kind.

Ag_2CrO_4 and $Ag_2Cr_2O_7$ (Fig. 15) do not line up with one another, nor with the other silver salts; this is to be expected, as is suggested for the potassium salts. $CaWO_4$ and $CaTiO_3$ seem, like $PbMoO_4$ in Fig. 14, unaccountably out of harmony with their neighbors. There is the same break in the direction of the shift line when

going from CaCrO_4 to CaCr_2O_4 (Fig. 15), and also from BaCrO_4 to BaCr_2O_4 (Fig. 16), as in the corresponding magnesium salts. The fact that the *first* (short wave) MgCrO_4 maximum, the *second* CaCrO_4 , and the *third* BaCrO_4 are on the shift lines in Figs. 14, 15, and 16, confirms the suggestion that these are corresponding peaks. (See the third shift line for the bivalent chromates, Fig. 12.) The "corrected" values, only, are shown in Fig. 15 for CaCr_2O_4 , obtained from the values for the "rock-salt" surface as

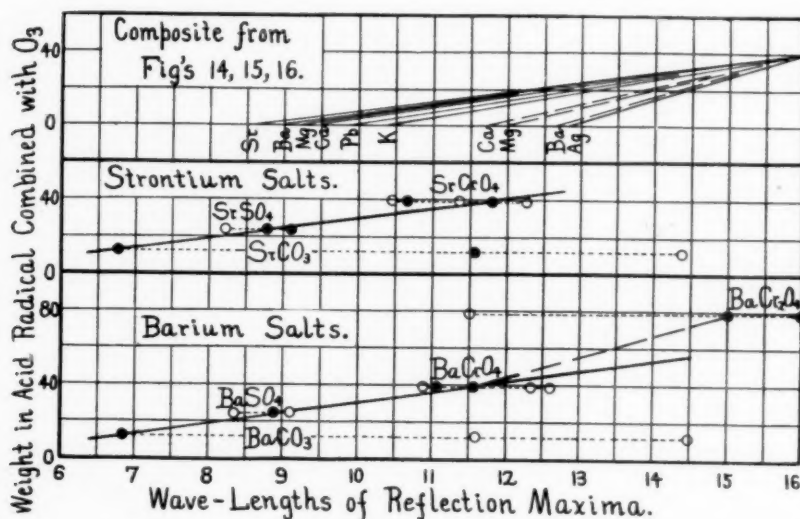


FIG. 16

indicated above. The 11.5μ point in BaCr_2O_4 is due to the presence of BaCrO_4 , as mentioned above. The explanations of the significance of the different kinds of plotting points, as given on Figs. 12 and 15, apply to Figs. 12 to 16, inclusive. The strontium salt shift is also shown on Fig. 16. At the top of this figure are plotted all the shift lines from Figs. 14 to 16, inclusive, from a common point, on the same scale as the original lines. Solid lines correspond to solid, and broken to broken.

As in the case of the composite of shift lines in Fig. 13, not much dependence can be placed on the relative location of two adjacent shift lines. There is no question, however, that the

broken lines are considerably steeper than the solid; this, as indicated above, is to be expected.

SUMMARY

1. Reflection curves for the available salts of the chromium acids have been determined in the region $1.5\ \mu$ to $15.0\ \mu$ or $16.0\ \mu$. The short wave-length portions of these curves are omitted here, because the reflection is constant in that region.

2. One surface was a polished crystal, which should be examined further with polarized energy. Some surfaces were made from the powdered salt, compressed against a steel plate, and polished; others were pressed against glass, to avoid polishing. Still others (including those strongly hygroscopic) were pressed against rock-salt cover plates, and the reflection measured without removing the cover plates. This form of surface may prove valuable for very hygroscopic salts, but its errors must be investigated further than has been done in the present work.

3. The dichromates show two complex maxima, in the regions $11.0\ \mu$ and $13.5\ \mu$, respectively. Each of the other salts shows only a single complex maximum; these maxima are in the region $11.0\ \mu$ to $12.0\ \mu$ for all but the chromites, in which they are from $15\ \mu$ to $16\ \mu$. In general, the salts of any one type have the same number of peaks in each complex maximum.

4. One salt, K_2CrO_4 , ought to prove a good source of *Reststrahlen*, with a mean wave-length of about $11.0\ \mu$.

5. When salts of one type, only, are compared with one another, all (with the exception of the chromites) show an approximately linear shift of the resonance region toward the long waves, with increasing atomic weight in the base. This shift holds, not only for resonance regions as a whole, but, in most cases, for individual peaks in complex maxima.

6. Representative shift lines for all of these types of salts, as well as for other types taken from the data of other observers, suggest that each type of salt has its own characteristic rate of shift.

7. A rate of shift enormously greater than the above is shown for all the salts of any one base, when the shift is plotted against that fractional part of the weight of the characteristic element in the acid radical, which is united with three atoms of oxygen.

8. Although the chance for error makes the exact location of shift lines of this sort much less determinate than that of shift lines of the first sort, it seems likely that the rate of shift is characteristic of salts of any one base. It is evident, however, in the case of the chromates and chromites concerned, that the shift due to replacing one chromium atom by two is much less rapid than if the one atom were replaced by another of twice its atomic weight.

9. The shifts of reflection maxima, as pointed out by Pfund, Coblentz, and Morse, are therefore confirmed for salts of the chromium acids, and further relations are pointed out.

The author is indebted to nearly everyone in the department of physics of Columbia University, where this work was done, also to several members of the departments of chemistry and mineralogy, for suggestions or help of various kinds. He is especially indebted to President E. F. Nichols of Dartmouth College, who set the problem and suggested many of the methods employed in its solution, and who has so kindly kept in touch with it as far as possible, since leaving Columbia for Dartmouth.

SYRACUSE UNIVERSITY

October 12, 1911

NOTES ON BAND SPECTRA BY W. RITZ¹

By PIERRE WEISS

I. MECHANISM OF EMISSION OF BAND SPECTRA

In the paper² in which Ritz studies a simple electromagnetic mechanism emitting series spectra, he states on p. 673 (*Œuvres*, p. 112):

These theories are not applicable to band spectra. I will only say in this connection that they might perhaps be ascribed to closed rings or polygons consisting of the elementary magnets under consideration, on the assumption that such formations play an important rôle in the construction of the atom, and that they must first be touched off by the electrical or chemical processes producing the light before a series spectrum can come into existence.

Among the papers left by Ritz there has been found a small sheet bearing some equations and a rough draft of the theory of this mechanism of emission of band spectra, which I shall attempt to expand.

Let us recall that the organ of emission of *series spectra*, conceived first by him as formed of magnetic and non-magnetic rods, juxtaposed in a straight line, may be realized in different ways. Ritz preferred to regard³ the small magnetic rods as produced by solids of revolution charged with electricity at their surface and having a rapid rotational motion around their axis. He had taken into account particularly that for any solids of revolution there can be found a superficial distribution of electricity which renders them equivalent to systems of two magnetic poles situated on the axis. When the magnetic poles approach the surface, the electric density increases indefinitely in their vicinity and the surfaces carrying the electricity become practically equivalent to point charges. These solids are alternately positive and negative, and endowed

¹ Note added to the *Œuvres de W. Ritz*, published by the Société suisse de physique, (Gauthier-Villars, 1911). Translated from the MS from M. Weiss.

² "Magnetische Atomfelder und Serienspektren," *Annalen der Physik*, **25**, 660, 1908; *Œuvres de W. Ritz*, chap. vii, p. 98.

³ *Op. cit.*, p. 670.

with rotations in opposite directions. They are fixed each to the other, in the form of a linear chain, by their electrostatic attraction. Ritz had thought that the non-magnetic rods, required also by the theory of series spectra, might be bodies similarly charged but deprived of rotation, and then, going a step farther, that the vibrating electron and the free electric pole at the extremity of the file of rods are one and the same thing.

Disregarding now the non-magnetic rods, let us consider a file of magnetic rods. We may assume that when it is subjected to a tension a^2 it is capable of vibrating in a manner analogous to that of a cord, or rather that of a chain.

There prevails along this cord a magnetic field H directed lengthwise, and it carries equidistant electric charges. Let us assume that these charges set up circular vibrations around the axis under the combined influence of the tension a^2 and the field H . (Ritz's notes say nothing in regard to the reason why the effect of the field on the adjacent positive and negative charges does not neutralize them. We may perhaps invoke for this purpose a difference of configuration of the positive and negative charges, which has been assumed elsewhere. Those occupying a more extended place would be, for example, partially outside the field.)

The vibratory state is then expressed by

$$\left. \begin{aligned} y &= A \sin \frac{\mu \pi x}{a} \sin \nu t \\ z &= A \sin \frac{\mu \pi x}{a} \cos \nu t \end{aligned} \right\} \quad (1)$$

where a is the distance between two consecutive knots for the fundamental vibration, and $\nu:2\pi$ the frequency. The equations of motion of an element of cord, dx , of mass μdx , and of charge ϵdx , will contain the term of inertia and the forces proceeding from the magnetic field and from the tension of the cord:

$$\left. \begin{aligned} \mu \frac{\delta^2 y}{\delta t^2} + \epsilon H \frac{\delta z}{\delta l} - a^2 \frac{\delta^2 y}{\delta x^2} &= 0 \\ \mu \frac{\delta^2 z}{\delta t^2} - \epsilon H \frac{\delta y}{\delta l} - a^2 \frac{\delta^2 z}{\delta x^2} &= 0 \end{aligned} \right\} \quad (2)$$

from which, substituting (1), twice the same equation:

$$\mu \cdot v^2 + \epsilon \cdot v \cdot H - \frac{\mu^2 \pi^2}{a^2} a^2 = 0 \quad (3)$$

in which H can also be replaced by $-H$, then

$$v = \pm \frac{\epsilon H}{2\mu} \pm \frac{\epsilon H}{2\mu} \sqrt{1 + \frac{4m^2 \pi^2 \mu}{\epsilon^2 H^2 a^2}}. \quad (4)$$

The solutions corresponding to the two positive signs and to the two negative signs are alone acceptable. In placing $\frac{4\pi^2 a^2 \mu}{\epsilon^2 H^2 a^2} = k^2$, a number which is small when the tension of the cord has a subordinate rôle with respect to the field, we have

$$v = \frac{\epsilon H}{\mu} \left[1 + \frac{m^2 k^2}{4} - \frac{m^4 k^4}{16} + \dots \right]. \quad (5)$$

For $m=0$, we find the frequency of a charge describing a circle in the field H . If we stop with the second term, we have Deslandres' law, with $v_0 = \frac{\epsilon H}{\mu}$ for the head of the band. If we retain the third term, v increases less rapidly, as experiment requires.

Ritz is here brought to choose between a rectilinear file and a closed ring. He gives the preference to the latter in the following terms: "If there are two extremities, the lines would have to be first simple ($m=1, 2, \dots$), for as m increases, the different vibrations will correspond accordingly as we are at the extremities or the center. Consequently, circular ring."

Since v increases with m , the band has the head on the red side. To obtain decreasing values, it is necessary to assume a^2 negative. The ring, instead of being extended, is compressed in the direction of the periphery.

The separation between two consecutive lines is given from the complete formula (4) by

$$\frac{dv}{dm} = \frac{v_0}{2} \frac{mk^2}{1 + m^2 k^2}.$$

It increases more slowly than Deslandres' law indicates, and that is in accord with the experiment. But the separation does not

cease increasing. The formula does not give then the maximum of separation of the experiments of Kayser and Runge¹ on the spectrum of cyanogen.²

Among some other notes of Ritz there is the trace of numerous attempts to find the best empirical formula with three constants representing these experiments of Kayser and Runge. These notes seem to be prior to his ideas on the electromagnetic origin of spectra and are accordingly only indirectly related to the above. He tries particularly

$$\nu = a + bm^2 \sqrt{1 + cm^4}$$

and the first three terms of its development

$$\nu = a + bm^2 + cm^6,$$

and finds that the term in m^6 varies too rapidly. He tries

$$\nu^2 = a + bm^2 + cm^4$$

and

$$\nu = a + bm^2 + cm^4.$$

He finds this last formula preferable to the others, and notes in this connection that "*from the 160th line the functions $\nu=f(m)$ and $\nu^2=f(m)$ behave in a manner not regular.*"

We shall revert to this point. He tries further

$$\nu^2 = \frac{a + bm^2}{1 + cm^2},$$

and the error is a little larger than formerly.

In a conversation Ritz expressed an idea which relates to the mechanism of emission what he calls "the irregular character of the function ν for the lines of high order." He expressed himself about as follows:

There are in certain bands a considerable number of lines whose position is determined with exactness; but, whatever the empirical law by which we

¹ *Wiedemanns Annalen*, **38**, 80, 1889.

² The same notebook also contains the following information, referring to another possible solution of the problem, in which the tension α^2 is not involved: "Beyond the constant magnetic field which it produces for its whole length, a ring can still be submitted to exterior magnetic fields, variable from point to point, and weak with respect to the first."

seek to represent the distribution of the lines in these bands, there comes a time when for a number of high order of lines this law fails. If we have recourse to a graphical representation, the curve turns short with an abruptness which the usual formulae do not give.

Let us assume that the part of the atom whose vibrations emit band spectra has a structure analogous to that of a chain composed of links of known length. One would understand then very well that the vibrations are produced for the greatest part of the phenomenon as if the chain were a continuous structure, while for wave-lengths of nearly the same length as the link (or for certain particular values in relation with it) the numbers of vibrations are influenced by the finite length of the element.

II. STRUCTURE OF THE BANDS

To the question, "Is it not established that the bands have sometimes two 'heads,' one on the side of large wave-lengths and the other on the side of small wave-lengths?" (hypothesis of Thiele¹), Ritz replied merely, "That idea is not tenable."

The tables of numbers found in his notes show that this conviction is based also on the study of the bands of cyanogen observed first by Kayser and Runge,² and later by Jungbluth,³ with heads at λ 3883.56, 3871.53, 3861.85, and 3854.85.

In a few words the status of the matter is this: King,⁴ having discovered new heads directed from the side of short wave-lengths, has believed it possible to consider them as "tails" corresponding to the "heads" previously known, and has associated them by making the bands overlap each other. As a proof of this co-ordination, he gives numerical relations between the wave-lengths of the heads and tails. They are contained in the following table:

T_n	Q_n	T_n/Q_n	T_n	Q_n	T_n/Q_n
3590.52	3203.84	1.12069	3883.60	3465.69	1.12059
3585.99	3180.58	1.12746	3871.59	3433.17	1.12770
3584.10	3160.32	1.13409	3861.91	3405.04	1.13417

The value of this table as a demonstration seems to me small. According to Deslandres' law, which is applicable to the heads of

¹ *Astrophysical Journal*, **6**, 65, 1897.

² *Wiedemanns Annalen*, **38**, 80, 1889.

³ *Astrophysical Journal*, **20**, 237, 1904.

⁴ *Ibid.*, **14**, 323, 1901.

bands of a series, as well as to the lines of a band, the distances between the successive heads, measured on a scale of frequencies, form an arithmetical progression. Suppose that we associate two series of bands turned in opposite directions, and both obeying this law, but entirely independent as to their origin. If the ratios of the two arithmetical progressions are close, as frequently happens,¹ the distances between the heads and tails will also form an arithmetical progression (criterion of dependence quoted by Jungbluth). It will be the same whatever two bands are taken to start with; and this will happen according as the ratios will be of the same or of contrary sign, when the first bands are displaced in the same or in contrary sense.

In the first approximation, the quotient of the frequencies will vary, in the same cases, in arithmetical progression. This is what King finds. In regard to the great similarity of the series of successive bands, we should not know how to attach any importance to the fact that this quotient passes twice approximately through the same three values.

This argument appears, nevertheless, to have had sufficient weight in the conviction of Kayser,² who considers it certain that King has found the tails corresponding to the heads, and that consequently the hypothesis of Thiele is correct.

Jungbluth proposes to test this hypothesis by making new measures on a part of the bands formerly known. To discuss them (Fig. 1),³ he uses as abscissas the wave-lengths, and as ordinates the difference of wave-lengths of two successive lines. The curves which he thus obtains for four of the bands of cyanogen proceed from their heads T_1 , T_2 , T_3 , and T_4 in an approximately parabolic manner, which corresponds to Deslandres' law $\nu = A + (Bm + C)^2$, where ν is the frequency and m a whole number; but for the lines of high orders the curve is distinctly below the parabola and the separation of the consecutive lines passes even through a maximum. These experimental curves are continued in dots and

¹ Ch. Fabry, *Journal de physique*, **4**, 245, 1905.

² *Handbuch der Spectroscopic*, **2**, 487.

³ The figure given here is Jungbluth's redrawn on the basis of the tabular values contained in his paper.

seem to end naturally, in the original drawing by Jungbluth, for the last three bands with tails Q_2 , Q_3 , Q_4 indicated by King. For the first, there being no head according to King in the region where Jungbluth expects it, he carries the curve on and thus determines

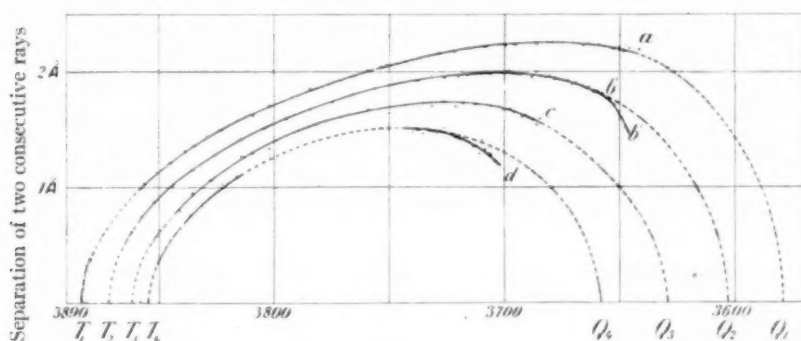


FIG. 1

the position of the tail Q_1 in a region where it is not observable on account of the presence of an intense band.

Omitting this, we have:

	Heads according to Jungbluth	Heads accord- ing to King	Assumed Tails
T_2	3871.53	4152.93	Q_2 3603.12
T_3	3861.85	4158.22	Q_3 3628.98
T_4	3854.85	4165.54	Q_4 3658.27

The co-ordination of the heads and tails according to Jungbluth is therefore in direct contradiction to that of King. Moreover, according to Jungbluth, the complete bands of King overlapping each other are replaced by bands fitting one within the other (Fig. 2).



FIG. 2

Jungbluth, who expressly notes this circumstance, does not fear to add that, taken in connection with the numerical relations of King, it brings a new confirmation to King's views.

To discover exactly what is the import of the experiments of Jungbluth, I have marked on the drawing (Fig. 1) the points observed. The experimental part, in heavy line, ends for the four bands in a, b, c, d . For two of the bands, at b , and at d , it is separated from the part extrapolated by Jungbluth, represented by a dotted line, by a greater curvature, seeming to confirm the idea of Ritz, and rendering impossible the assignment of the tails made by Jungbluth.

But if we compare the experiments of Jungbluth with that of Kayser and Runge, the agreement which is good as far as b' ceases. It is easily seen that Jungbluth has at b' passed inadvertently to the lines of a neighboring band, which are placed in respect to those that he has followed to that point somewhat as the lines of a vernier are to those of the principal scale. Moreover, Jungbluth suppressed in his drawing the portion $b'b$. Definitively for the four bands, the correlation between the heads and tails is admissible rigorously for two of them (T_2-Q_2 ; T_3-Q_3).

Ritz's idea of the irregular nature of the function ν for the lines of high order which rests on the sharpness of the turn at b' has in part as its origin an error of Jungbluth.

It seems, nevertheless, that as a result of the paper by Jungbluth the conviction has become general that the hypothesis of Thiele is correct. In 1905 A. Hagenbach¹ expressed this in a monograph on band spectra. It has not been remarked that in reality the *conclusions* of Jungbluth at the end of his paper are much less affirmative than his *curves*.

We find in Ritz's notes the following: "The tails according to King, particularly the one at λ 3603, are impossible, because they are composed of lines relatively intense with almost *constant differences*, while the differences ought to increase very rapidly toward the head of the band."

This remark is very probably suggested by an examination of the plate of Kayser and Runge² on which it is easy to recognize the appearance described by Ritz. It is possible to measure the distance of the lines to about 0.5 Å, which carries the arc of the

¹ Wüllner-Festschrift, 133, 1905.

² Akad. Berlin. Phys. Abh. nicht zur Akad. gehör. Gelehrter, 1, 44, 1889.

corresponding curve well outside the limits of the figure. The same is visible on the plate of Jungbluth (*op. cit.*).

This argument seems definitively to destroy what remains of probability in the assumptions made by Jungbluth. We have already done justice incidentally to the argument which Jungbluth deduces on the ground that the *lengths* of the bands vary in arithmetical progression. Let us mention that, on the contrary, Ritz notes carefully, as an important fact, the arithmetical progression, pointed out by Jungbluth, of the maxima separations of the lines of the four bands (2.25; 2.00; 1.75; 1.5 Å). This fact retains its value independently of every hypothesis as to the existence of one head or of two heads.

We may then conclude that the hypothesis of Thiele is strengthened by:

1. The existence of heads directed in the two senses.
2. The existence of a maximum in the separation of the lines.

But we have not been able to continue the demonstration of this hypothesis up to the present time, either by the possibility of co-ordinating without confusing the heads and tails, or by pursuing the decrease of the distance of the lines in an interval sufficiently extended beyond the maximum. The separation of the lines in the region of the tail at λ 3603 disproves it strictly.

Ritz's idea is not in contradiction with the facts. But the indications in his favor which remain with regard to the four bands of cyanogen are slightly diminished after suppressing the faulty part, *b'b*, of Jungbluth's.

It would be of great interest to make new determinations on bands composed of a large number of lines and, perhaps, to resume the discussion of the data already found.

ZURICH, SWITZERLAND
March, 1911

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